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ON THE CONSTITUTION OF SODIUM ACET-ACETIC ETHER.

BY ARTHUR MICHAEL.

There are few reactions in organic chemistry that have been investigated with such different results as that of chlorcarbonic ether on sodium acet-acetic ether. Briefly mentioned by Ehrlich,[1] it was more carefully examined by Conrad and Guthzeit,[2] who supposed the product formed to be acet-malonic ether, although they found it to be a neutral oil and were unable to replace the methin-hydrogen in it by sodium. These chemists also examined the behavior of chlorcarbonic ether towards sodium malonic ether and obtained methin-tricarbonic ether, which showed a neutral character towards bases. To explain these results it was supposed that the neutral properties of these compounds are due to the grouping of three negative radicles on one carbon, an explanation which, even at that time, seemed very improbable. Lange[3] subsequently examined the action of acetyl chloride on sodium malonic ether and assumed, apparently without further examination, that the product thus formed was identical with the acet-malonic ether of Conrad and Guthzeit.

Theoretical considerations, relating to the constitutions of acet-acetic ether and its sodium derivative, induced me[4] to re-examine

[1] Ber. d. chem. Ges. **7**, 892. [2] Ann. Chem. (Liebig) **214**, 31.
[3] Ber. d. chem. Ges. **20**, 1325.
[4] This Journal **10**, 158, and more fully in J. prakt. Chem. [2] **37**, 473.

the work of Conrad and Guthzeit and Lange. I found the product from sodium acet-acetic ether to be, as described, a neutral oil, yielding sodium acet-acetic ether when treated with sodium ethylate; but the substance obtained by Lange from sodium malonic ether and acetyl chloride possesses entirely different properties, it having a strongly developed acid character and forming a stable sodium derivative when treated with sodium ethylate. In fact, Lange's compound represents the real acet-malonic ether, whereas the product obtained from sodium acet-acetic ether very probably has the constitution $CH_3—\overset{\displaystyle OCOOC_2H_5}{\overset{|}{C}}—CH—COOC_2H_5$. It was also shown that Conrad and Guthzeit made an error in ascertaining methin-tricarbonic ether to be neutral, as it dissolves even in aqueous sodium carbonate to form a stable sodium derivative. Shortly after my paper, Claisen and Zedel[1] published a brief note stating that carb-ethoxyl-acet-acetic ether is formed from acet-acetic ether by replacing both of the methylene hydrogens by carb-ethoxyl, and therefore represents the compound $CH_3—CO—C\equiv(COOC_2H_5)_3$, a constitution which also explains its neutral character; also that methin-tricarbonic ether is in reality carbin-tetracarbonic ether, which, according to these chemists, agrees better with its properties than the constitution hitherto accepted. In view of the fact that methin-tricarbonic ether possesses strong acid properties, it might have been safely assumed at the time that Claisen and Zedel had made some experimental mistake, as this property absolutely precludes the structure which they supposed to accord better with its properties. In fact Claisen[2] corrected his statements in the same number of the *Berichte*, having found that later vapor-density determinations of carb-ethoxyl-acet-acetic and methin-tricarbonic ethers show conclusively that the compounds are mono-derivatives of acet-acetic and malonic ether.

The constitution I gave to carb-ethoxyl-acet-acetic ether seems to have been pretty generally accepted, and only very recently has the subject been further investigated, when J. U. Nef,[3] in a paper on the constitution of acet-acetic ether, concluded from experimental work of his own that Claisen's first supposition is correct and therefore the substance has the structure $CH_3—CO—$

[1] Ber. d. chem. Ges. **21**, 3397. [2] Ibid. **21**, 3567. [3] Ann. Chem. (Liebig) **266**, 52.

$C(COOC_2H_5)_2$. Nef's conclusion is based on the formation of some acet-malonic ether in the action of chlorcarbonic ether on sodium acet-acetic ether; on two combustions of carb-ethoxyl-acet-acetic ether purified by a method of his own, and "namentlich auf Grund der gemachten Erfahrungen beim Dibenzoyl- und Diacetyl-acetessigäther."[1] He rejects Claisen's and my work, owing to our having worked with an impure substance, and claims to have definitely settled the problem of the action of chlorcarbonic ether on sodium acet-acetic ether. Nothing in Nef's work appeared to the writer to justify such a conclusion. The differences between the carbon and hydrogen percentages of a mono- and di-derivative of acet-acetic ether do not amount in either case to one per cent., and in this research of Nef quite a number of analyses are stated which differ over one per cent. in carbon from the amount required by theory. Again, the amount of acet-malonic ether contained in carb-ethoxyl-acet-acetic ether, purified by repeated fractionation *in vacuo*, could not possibly have had any noticeable effect on my analyses; while the formation of diacetyl-acet-acetic ether is quite irrelevant to the subject in question, as acetyl chloride in its action on sodium malonic ether forms di- as well as mono-acetyl-malonic ether, whereas chlorcarbonic ether acting on the same compounds yields simply a mono-derivative, and, finally, the constitution I assigned to carb-ethoxyl-acetic ether accords with its properties. I had further reason to believe Nef's conclusion incorrect as I had previously examined the action of chlorcarbonic ether on sodium ethyl-acet-acetic ether, and of acetyl chloride on sodium ethyl-malonic ether, and isolated isomeric products as results of these reactions, which differed entirely in their behavior towards certain reagents. Since only one carb-ethoxyl can be introduced in ethyl-acet-acetic ether, and the compound thus formed is not only different from acet-ethyl-malonic ether, but showed by its decompositions that the introduced carb-ethoxyl is joined with oxygen, these facts evidently pointed to a similar constitution for carb-ethoxyl-acet-acetic ether. It seemed to me of importance that inaccurate observations bearing on questions so important to organic chemistry as the constitution of acet-acetic and malonic ethers, their homologues and sodium derivatives, should not be allowed to influence the judgment of chemists on the constitution of these substances, and I

[1] Ann. Chem. (Liebig) **266**, 106.

have therefore repeated that part of Nef's work which bears on these questions. I find my surmise of the imperfectness of this work is correct, both as regards the observation of facts and the analyses. I have also repeated my former, as yet unpublished work, with the ethyl homologues of the compounds described in my previous paper; and to confirm these results still further, the corresponding methyl derivatives were prepared and their properties examined. Before describing the experimental part of my work I wish briefly to explain my views on the constitution of acet-acetic ether, its homologues and their sodium derivatives.

In a former paper[1] on the constitution of sodium acet-acetic ether I called attention to the two reactions that indicate a carbinol constitution for acet-acetic ether and levulinic acid, but I further pointed out that these reactions are also explained by the assumption that these compounds contain a ketone-carbonyl, if they are considered as the final result of additions and subsequent eliminations.[2] There was therefore no valid reason for assigning to acet-acetic ether any constitution other than $CH_3—CO—CH_2—COOC_2H_5$, but in regard to its sodium derivative the formation of carb-ethoxyl-acet-acetic ether from it, as well as the results obtained by the action of carbonyl chloride and alkylene halides, are only explainable by $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$ representing the structure of its sodium derivative. As sodium acet-acetic ether is formed by the direct action of sodium on acet-acetic ether, it must be assumed that the product $CH_3—CO—CHNa—COOC_2H_5$ is formed at first, but, owing to the affinity of the strongly negative ketone oxygen for the very positive sodium, a molecular rearrangement immediately takes place, when the sodium passes over to oxygen with formation of the unsaturated compound $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$. It is, however, only the metallic derivatives of acet-acetic ether that possess this constitution, as when the metal is replaced by hydrogen a rearrangement of atoms takes place, common to all known instances where hydroxyl is joined to an unsaturated carbon in a fatty compound, and the unstable $CH_3—\dot{C}OH—\dot{C}H—COOC_2H_5$ imme-

[1] J. prakt. Chem. [2] **37**, 473.

[2] Bredt (Ann. Chem. (Liebig) **256**, 314) has since endeavored to sustain the lactone constitution of levulinic acid, but I have lately published (J. prakt. Chem. [2] **44**, 113) a paper on this subject and have shown experimentally that the ketone constitution is the only one known that agrees with the properties of this acid.

diately passes over into $CH_3—CO—CH_2—COOC_2H_5$. The above constitution of sodium acet-acetic ether had been previously assigned to this compound by Geuther, as a direct result of his conception of acet-acetic ether as $CH_3—COH=CH—COOC_2H_5$, but his views and mine are in all other respects essentially different. Geuther, for instance, gave ethyl-acet-acetic ether the constitution $CH_3—COC_2H_5=CH—COOC_2H_5$, although it had been proved beyond all doubt that when ethyl is introduced into acet-acetic ether it is joined to carbon and not to oxygen. To explain the formation of a carbon-homologue by the action of ethyl iodide on $CH_3—\dot{C}ONa—\dot{C}H—COOC_2H_5$, attention was called to the probability of the reaction being the outcome of an addition and subsequent elimination of sodium iodide; and not, as was generally supposed at the time, of a direct substitution. According to this interpretation the unsaturated carbons of sodium acet-acetic ether are in such a positive-negative condition as gives them a sufficiently strong affinity for ethyl and iodine to unite with ethyl iodide, the negative iodine uniting with the relatively positive unsaturated carbon and the positive ethyl with the relatively negative carbon — reactions that are expressed by the following equations:

$$CH_3—\overset{+}{\dot{C}}ONa—\overset{-}{\dot{C}}H—COOC_2H_5+\overset{+}{C_2H_5}\overset{-}{I}=$$

$$CH_3—\overset{+}{C}\begin{matrix}\diagup I\\ \diagdown ONa\end{matrix}^{-}+\overset{+}{C}<\begin{matrix}C_2H_5\\ H\end{matrix}^{-}—COOC_2H_5=$$

$$CH_3—CO—CHC_2H_5—COOC_2H_5+NaI.$$

A large number of other classes of compounds which like acet-acetic ether can form sodium derivatives, as malonic and phenyl-sulphon-acetic ethers or nitro-methane, were also considered, and the general conclusion drawn that in no organic compound containing oxygen and sodium can a stable form of the compound exist in which the metal is directly joined to carbon.

The explanation given above for the formation of alkyl-acet-acetic ethers, by addition of alkyl and iodine to the unsaturated carbons and subsequent elimination of sodium iodide, led me to consider the rôle which addition plays in organic chemistry, and it was inferred that far more reactions are the results of addi-

tions than was generally supposed.[1] This subject was fully considered at the time,[2] but, as illustrations, I shall here discuss several reactions from this point of view. Methyl iodide unites readily in the cold with methyl sulphide to form trimethyl-sulphonium iodide, and this property of the sulphur of adding methyl and iodine makes it appear highly probable that methyl iodide in reacting on potassium sulphide also does it by the addition of methyl and iodine to sulphur. It can be shown that the facility with which sulphur adds methyl iodide depends on its being in a relatively positive condition, but as potassium is far more positive than methyl, the sulphur of potassium sulphide must be relatively more positive than the sulphur of methyl sulphide and should therefore unite with methyl iodide far more readily. The usual interpretation, therefore, that methyl iodide and potassium sulphide give potassium-methyl sulphide by substitution is not only a pure assumption, but is very improbable. The new conception of the reaction may be represented as follows:

$$K-S-K + CH_3I = K-\overset{\overset{CH_3\,I}{\vee}}{S}-K = K-S-CH_3 + KI.$$

A sulphur atom, like that of methyl sulphide or of potassium sulphide, which has the power of adding alkyl halides was called relatively positive sulphur, and it probably exists in this state in KSCN. In this salt nitrogen very likely also is in a relatively positive condition, *i. e.* it may add alkyl iodides, but the sulphur, owing to its being joined directly to potassium, has a greater additive power than the nitrogen. A different condition occurs in silver cyanate, as oxygen adds under no conditions whatsoever and addition can therefore only take place on the positive nitrogen:

$$K-S-CN + C_2H_5I = K-\overset{\overset{I\,C_2H_5}{\vee}}{S}-CN = C_2H_5S-CN + KI.$$

$$Ag-O-CN + C_2H_5I = Ag-O-C-\overset{\overset{I\,C_2H_5}{\vee}}{N}=C_2H_5-NCO + AgI.$$

[1] "Ueberhaupt scheint die besprochene Reaction gerade geeignet, um zu zeigen dass man bei Reactionen, wo die Bildung eines intermediären ungesättigten Produktes denkbar ist, nicht das Endresultat der Reaction im Licht einer vorgefassten Meinung beurtheilen darf." That this caution in my paper (J. prakt. Chem. [2] **35**, 356) on the addition of sodium acet-acetic and malonic ethers to the ethers of unsaturated organic acids was timely is evident from the papers and controversies of Auwers, Bischof, Zelinsky and others that appeared several years after the above communication was published.

[2] J. prakt. Chem. [2] **37**, 507–522.

The existence of potassium sulpho-cyanate, KSCN, and of silver cyanate, AgOCN, does not imply the stability of the corresponding free acid, as hydrogen is not sufficiently positive to give permanence to such negative structures. Molecular rearrangements, therefore, take place when the metal is replaced by hydrogen, which passes over to nitrogen, and the stable forms, SCNH and OCNH, result.

A considerable number of reactions were discussed in the light of this hypothesis, and not a few hitherto unintelligible results were shown to be explainable by it. In fact the great majority of reactions were considered in which tautomerism, desmotropism or the pseudoform hypothesis had been assumed to explain the apparent existence of two structures for the same substance. In using these hypotheses, which were really rather names to imply what seemed to be facts, than explanations, a most important element had been overlooked, *i. e.* that the replacement of hydrogen by a more positive metal in those compounds that Laar supposed to have a hydrogen constantly changing its position, might cause a molecular rearrangement forming a different structure, which is stable only for the metallic derivative, as the replacement of the metal in it by hydrogen is followed by a molecular readjustment to the original constitution. This important factor, considered in connection with the phenomenon of addition, leaves, as far as I am aware, no instance where such an hypothesis is necessary, and according to this view tautomerism or desmotropism, in the sense in which that term is ordinarily used, does not exist. As this explanation of the phenomenon is materially different from previous conceptions, as is also the line of investigation it suggests, I propose to designate it by the expression *merotropy*.[1]

Action of Chlorcarbonic Ether on Sodium Acet-acetic Ether.

12.6 grams granulated sodium were brought under 600 grams pure ether, in a flask connected with an inverted cooler, and 73 grams acet-acetic ether (purified by several distillations *in vacuo*) were added in small portions and under constant shaking, so that it took about an hour before the addition of acet-acetic ether was completed. The ether was heated to boiling during the operation and finally the flask was put into a vessel of warm water and shaken for a half-hour, when the conversion into sodium acet-

[1] See J. prakt. Chem. [2] **42**, 19; **44**, 125.

acetic ether was finished. A considerable quantity of sodium derivative had separated and the contents of the flask became thick on cooling. The flask was then well cooled off in ice-water and 59.6 grams chlorcarbonic ether gradually added from a drop-funnel, under constant shaking of the flask, which was then allowed to stand in cold water for a day. A reaction took place immediately and the greater part of the sodium derivative passed into solution, when only a small amount of the chlorcarbonic ether had been added. After standing twenty-four hours the ethereal solution still showed a slight alkaline reaction, which did not disappear on standing a longer time. The ethereal solution was shaken out several times with water and then dried over sodium sulphate.

The ether was distilled off and the residual oil, repeatedly fractionated *in vacuo*, gave unchanged acet-acetic ether and a good yield of the so-called acet-malonic ether. For analysis the latter product was fractionated several times *in vacuo*, even after a constant-boiling liquid had been obtained.

I. 0.2535 gram substance, burned with $PbCrO_4$, gave 0.4954 gram CO_2 and 0.1629 gram H_2O.

II. 0.2162 gram substance, burned with $PbCrO_4$, gave 0.4228 gram CO_2 and 0.1383 gram H_2O.

	Theory for $C_9H_{14}O_5$.	Found. I.	II.
C	53.46	53.29	53.33
H	6.93	7.14	7.21

Boiling between these two ethers I obtained some oil, which I had intended to examine, but a long interruption of my work prevented me from studying this part of the reaction more carefully. Nef, making use of the observations described in my paper, succeeded in isolating some acet-malonic ether in this reaction, undoubtedly the principal part of the intermediate-boiling oil, and rejects the work done by Claisen and myself, as he thinks we worked with an impure product. I have since repeated the preparation of carb-ethoxyl-acet-acetic ether in the manner just described, and obtained by fractionation *in vacuo* a colorless oil, which boils without decomposition at 136° (20 mm. pressure, metal bath at 165°), and, even after several further re-fractionations, still gave a reddish coloration on addition of ferric chloride to its alcoholic solution, although the color was but

slight. Carb-ethoxyl-acet-acetic ether cannot, according to these results, be perfectly freed from acet-malonic ether by fractionating, but the proportion of that compound contained in a product purified in this way is so small that it is not much more than a trace, as I convinced myself by extracting the acet-malonic ether from it with aqueous sodium carbonate. The portions in the above preparation boiling over 100° *in vacuo*, and the almost pure carb-ethoxyl-acet-acetic ether were separately extracted, in ethereal solution, four times with aqueous sodium carbonate, then twice with dilute aqueous sodium hydrate, and the ether solution dried over sodium sulphate. On fractionation of these products *in vacuo* a carb-ethoxyl-acet-acetic ether was obtained which gave no coloration with ferric chloride, but the boiling-point remained unchanged, it being 136° under 20 mm. and 133° under 17 mm. The analyses of this oil gave the following results:

I. 0.2332 gram oil, burnt in open tube, gave 0.4507 gram CO_2 and 0.1435 gram H_2O.

II. 0.2732 gram oil, burnt in open tube, gave 0.5335 gram CO_2 and 0.1763 gram H_2O.[1]

III. 0.2386 gram oil, burnt with $PbCrO_4$, gave 0.4689 gram CO_2 and 0.1524 gram H_2O.

IV. 0.2050 gram oil, burnt with $PbCrO_4$, gave ——— gram CO_2 and 0.1350 gram H_2O.[2]

	Theory for Acet-carbin-tricarbonic ether.	Carb-ethoxyl-acet-acetic ether.	Found. I.	II.	III.	IV.
C	52.55	53.46	52.68	53.25	53.55	...
H	6.57	6.93	6.83	7.17	7.10	7.10

The small difference in the carbon and hydrogen percentages of acet-carbin-tricarbonic and carb-ethoxyl-acet-acetic ethers induced Claisen to determine the vapor-density of the compound *in vacuo*, according to Hofmann's method, as the molecular weights of the above compounds differ widely, viz. 274 and 202. Claisen states that his results leave no doubt that the compound cannot be a tricarbonic ether, but Nef[3] considers Claisen's results as inconclusive, owing to the assumed presence of acet-malonic

[1] Analyses I and II are given to show the great difficulty of obtaining accurate results by burning this substance in oxygen in an open tube. Analysis II was burnt in a platinum boat and the combustion-tube heated to an unusually high temperature, but even then the carbon is a little too low.

[2] The carbon was lost through an accident.

[3] Ann. Chem. (Liebig) **266**, 108.

ether in the product used by Claisen. It has already been shown that, under any circumstances, the amount of acet-malonic ether contained in a product obtained by fractionation *in vacuo* would have been too small to have had a noticeable influence on the results obtained by Claisen. However, Nef might easily have convinced himself that, even supposing the product which Claisen used for his density determinations to have contained the impossible proportion of 20 per cent. acet-malonic ether, it would not have been possible for that chemist to have gotten the results he states. To remove any uncertainty as to the molecular weight of carb-ethoxyl-acet-acetic ether I determined the vapor density of a product free from acet-malonic ether, according to Hofmann's method, using a tube about 1½ metres long and aniline vapor, with the following results:

$p = 0.024$ gram, $v = 58.3$ cc., $h_1 = 331$ mm. at 21°, $h_2 = 360$ mm., $B = 751.8$ at 15°.

Calculated for $CH_3-CO-C(COOC_2H_5)_3$.	For $CH_3\cdot C(OCOOC_2H_5)\text{-}CH\text{-}COOC_2H_5$.	Found.
274	202	200

Nef obtained his carb-ethoxyl-acet-acetic ether in a perfectly pure state by finally treating it with fuming nitric acid. Although I fail to understand why this operation is necessary, or even desirable, it was repeated, using a product which was already perfectly pure. 20 grams of the ether were gradually introduced into one and a half times its volume of fuming nitric acid (1.52), cooled off in a mixture of ice and salt, allowed to stand twenty minutes, during which time the escape of colored fumes was noticed, and then the solution thrown into ice-water. The oil which settled was separated from the supernatant liquid, water added to it, and then extracted with ether.[1] The ether solution was extracted three times with aqueous sodium carbonate (dilute sulphuric acid, added to this solution after extraction, gave fumes of nitrous acid), then three times with dilute potassium hydrate, finally once with water, and the ethereal solution dried over fused sodium sulphate. On fractionation, a product was obtained which boiled exactly at the same temperature as before this treatment, viz. 136° at 20 mm. pressure. I wish to correct here the statement made by Nef that carb-ethoxyl-acet-acetic ether is entirely unacted on by fuming

[1] Nef extracts directly with ether — obviously a mistake, as the products of decomposition may be extracted along with the carb-ethoxyl-acet-acetic ether.

nitric acid in the cold, as only 14 grams of the 20 used in the experiment were recovered, and on subjecting this product to a second treatment with fuming nitric acid it undergoes again a partial decomposition.

On analysis this supposed purer product gave the following result:

0.2317 gram substance gave, burned with $PbCrO_4$, 0.4551 gram CO_2 and 0.1532 gram H_2O.

	Calculated for $CH_3-COCOOC_2H_5-CH-COOC_2H_5$.	Found.
C	53.46	53.56
H	6.93	7.22

A vapor-density determination of this product was also made, according to the vacuum method of Hofmann, with the following results: $p = 0.0457$, $v = 64.2$ cc., $h_1 = 325$ mm. at 22°, $h_2 = 347$ mm., $B = 753.3$ mm. at 15°, from which results the molecular weight 200.6 is calculated. It may safely be inferred from the above results that the treatment of carb-ethoxyl-acet-acetic ether with nitric acid is superfluous, entailing as it does only a considerable loss of substance. The statement made by Nef in regard to the formation of acet-malonic ether in the action of chlorcarbonic ether on sodium acet-acetic ether I have found correct, although in my experiment it was far less than the amount he obtained. Unfortunately a small part of this substance was lost through an accident and I am therefore unable to state exactly the proportion formed, but I am sure that 10 per cent. is certainly rather above than below the amount.

In the introduction to his paper Nef[1] expressed his opinion that my conclusion in regard to the constitution of carb-ethoxyl-acet-acetic ether is very doubtful, as all that was known about the compound was its neutral behavior towards alkalies and that it could be decomposed by alcoholic potash into acetone and carbonic acid. This critic showed by such statements how carelessly he had read my paper, for in it he would have found part of the results which he published as new.

Ten grams carb-ethoxyl-acet-acetic ether were cooled off in ice and 3.4 grams powdered dry sodium ethylate, in proportion of equal molecules, added in small quantities at a time, as otherwise the reaction is quite violent, and the mixture well stirred after

[1] Ann. Chem. (Liebig) **266**, 57.

each addition. The product became very thick, even before all the sodium ethylate was in the flask, and to facilitate the action finally a small quantity of dry ether was added and the almost solid mass mixed as well as possible. After standing in a cold place for a day, water was added to the product, and as soon as the solid had dissolved the solution was extracted with ether. After drying over fused sodium sulphate the ethereal extract was fractionated and, after one gram of liquid boiling between 125°–135° passed over,—which contained carbonic ether as was shown by decomposing it by caustic potash—the thermometer rose rapidly to 178° (only 0.15 gram liquid passed over between these temperatures) when 4 grams acet-acetic ether distilled off. The thermometer then rose rapidly to 235°–240° when 1.7 grams undecomposed carb-ethoxyl-acet-acetic ether passed off, leaving a very small black residue in the boiling-flask. On acidulating the alkaline liquid, which had been extracted by ether, considerable carbon dioxide was evolved, and from the acid solution a very small quantity of an oil was extracted, but the amount, 0.05 gram, did not permit a further examination. Carb-ethoxyl-acet-acetic ether is therefore decomposed by dry sodium ethylate into sodium carbonate, some carbonic ether and acet-acetic ether. After reading Nef's paper I repeated this experiment, as I inferred from his statement that an almost quantitative decomposition into ethyl carbonate and sodium acet-acetic ether takes place in this reaction, and as the results of the second experiment confirmed those I had previously obtained, the equation given by Nef[1] therefore does not represent the reaction correctly.[2]

In my first paper I mentioned that phenylhydrazine acetate and hydroxylamine act on carb-ethoxyl-acet-acetic ether, and that a solid product was obtained by using the first-named reagent. This reaction was examined shortly afterwards with the following results: To an aqueous solution of 10 grams phenylhydrazine chlorhydrate and 15 grams sodium acetate, 10 grams carb-ethoxyl-acet-acetic ether and sufficient alcohol to effect its solution were added. After standing some hours an oil began to separate from the solution. This gradually increased in quantity for several days, when the solution was extracted with ether, the extract dried over calcium chloride and then evaporated *in vacuo*. On

[1] Loc. cit. 107.

[2] By using alcoholic sodium ethylate proportionately less carbonic ether is formed.

long standing *in vacuo* the residue gradually turned almost solid, and was first digested in the cold with about 20 cc. dry ether, and an insoluble residue filtered off, which was then extracted twice with the boiling solvent. On cooling the last two extractions, needles separated, which were filtered off and added to the insoluble part, and the ether extracts evaporated, when on standing *in vacuo* the residue became almost solid. It was again treated with a small quantity of ether, filtered from a few crystals, and, after evaporation of the ether, the residue crystallised five times from carbon disulphide. Long white needles were obtained which melt at 80°–81°, and are sparingly soluble in cold water, moderately soluble in cold, readily in boiling carbon disulphide, and very soluble in cold alcohol or ether. On analysis the following results were obtained:

I. 0.1355 gram substance gave 0.2953 gram CO_2 and 0.0845 gram H_2O.

II. 0.2158 gram substance gave 29.8 cc. N at 16° and 753 mm. pressure.

III. 0.2013 gram substance gave 27.2 cc. N at 13° and 746.7 mm. pressure.

	Theory for $C_6H_5-NH-NHCOOC_2H_5$.	Found. I.	II.	III.
C	59.99	59.46	...	...
H	6.66	6.91	...	...
N	15.55	...	15.81	15.77

The crystalline, insoluble residue from the above product was purified by several crystallisations from water, and consisted of white prisms that melt at 127°, that agreed in all their physical and chemical properties with phenyl-methyl-pyrazolone. As the appearance of this compound may have been due to the formation of acet-acetic ether, it seemed of interest to ascertain whether that compound gives the pyrazolone with phenylhydrazine acetate. On allowing an alcohol solution of the ether and acetate to stand several days, then evaporating the alcohol *in vacuo*, a crystalline residue was obtained that dissolved in water and gave a very good yield of phenyl-methyl-pyrazolone on careful neutralisation. Knorr[1] had previously noticed the formation of this pyrazolone by heating an acetic-acid solution of hydrazine and acet-acetic ether, but attributed its formation to the action of heat on the "hydrazone."

[1] Ann. Chem. (Liebig) **238**, 147.

Nef[1] obtained the compound melting at 81° by the action of free phenylhydrazine on carb-ethoxyl-acet-acetic ether, and believes that two molecules of it to one of acet-acetic ether are formed in the reaction; and he also noticed the formation of water. My observations on the formation of the compound indicated that its presence was rather due to a secondary reaction. I therefore made an experiment on the action of the free base after reading Nef's paper. Five grams pure carb-ethoxyl-acet-acetic ether were dissolved in 5 grams dry ether and 2.55 grams phenylhydrazine (in proportion of equal molecules) were added. The solution became only perceptibly warm, and gradually took a yellow-brown color, but it remained perfectly clear. Nef's observation in regard to the formation of water in this reaction is incorrect, and the addition of calcium chloride, which was used to facilitate the formation of water, is quite unnecessary. Nef washed the ethereal solution with alkaline and acid solutions, but I shall show farther on that this treatment is not desirable, as both acids and alkalies act on hydrazones of β-ketone acid ethers. After standing four days the ether was evaporated and the residue allowed to stand in a vacuum as long as the crystals that soon separated increased in number. By adding petroleum ether and warming the greater part of the oil dissolved, and the remaining crystals, afterwards crystallised from as little hot carbon disulphide as possible and dried, weighed 1.6 grams and melted at 76°–78°. After several recrystallisations from carbon disulphide they melted at 80°–81° and agreed in their properties with the above-described compound.

The petroleum ether from the crystals was evaporated and allowed to remain several weeks *in vacuo*, but no further separation of crystals was noticed, and it may therefore be assumed that the amount above stated (1.6 grams) represents approximately the quantity of the substance that is formed in the reaction, which should be no less than 6.5 grams if Nef's view were correct. On treating the oil with alkalies it could be separated into a soluble and insoluble portion, neither of which could be obtained in a pure state, but no acet-acetic ether could be detected in the soluble part. Free phenylhydrazine acts, therefore, on carb-ethoxyl-acet-acetic ether forming an acid and a neutral substance, and the compound melting at 81°; but, as the amount of the latter substance formed is comparatively small, the other products may result from the direct action of the base with the elimination of alcohol.

[1] Ann. Chem. (Liebig) **266**, 107.

Several experiments were made on the action of an alcoholic solution of hydroxylamine on carb-ethoxyl-acet-acetic ether, but as only a dark-colored oil was obtained which could not be purified, the reaction was not further studied.

The formation of the compound $C_6H_5NH—NH—COOC_2H_5$ by the action of phenylhydrazine acetate solution is of importance, as hitherto no instance is known where this mixture splits off carb-ethoxyl from derivatives of acet-acetic ether when this group is joined to carbon, whereas free hydrazine often acts as a base in such compounds. The above reaction is therefore a further proof of the constitution I originally assigned to carb-ethoxyl-acet-acetic ether, and indeed there is no property of the compound known which does not directly follow from such a structure.

Action of Acetyl Chloride on Sodium Malonic Ether.

This reaction was first studied by Lange,[1] who supposed the product he obtained to be identical with the neutral compound Conrad and Guthzeit had prepared by the action of chlorcarbonic ether on sodium acet-acetic ether.

In preparing this compound 7.2 grams finely granulated sodium were brought under 250 grams dry ether, and 50 grams malonic ether added in small quantities at a time. After no more hydrogen was evolved, even though the thick mass of sodium malonic ether was thoroughly shaken, the mixture was cooled off and 24.5 grams acetyl chloride added slowly from a drop-funnel. A reaction took place immediately, and, after a comparatively small amount of chloride had been added, the sodium derivative went into solution. On standing over night the solution showed a neutral reaction. About one-half of the ether was then distilled off, the remaining solution extracted with water, dried over calcium chloride, and, after the ether was driven off on a water-bath, the oil was fractionated *in vacuo*, as distillation under ordinary pressure caused considerable loss by decomposition. It was easy to separate three different liquids from the product of the reaction,—unchanged malonic ether, an oil boiling at 120° under 17 mm. pressure, and a higher-boiling liquid, the formation of which had been overlooked by Lange. Analyses of the product boiling at 120° gave the following numbers:

[1] Ber. d. chem. Ges. **20**, 1325.

I. 0.1842 gram oil, burnt in open tube, gave 0.3591 gram CO_2 and 0.1215 gram H_2O.

II. 0.2640 gram oil, burnt with $PbCrO_4$, gave 0.5182 gram CO_2 and 0.1880 gram H_2O.

	Calculated for $CH_3-CO-CH(COOC_2H_5)_2$.	Found. I.	Found. II.
C	53.46	53.16	53.51
H	6.93	7.22	7.16

Acet-malonic ether boils with slight decomposition under ordinary pressure, but without change *in vacuo*. It possesses strongly developed acid properties, dissolving readily in aqueous alkalies and even in aqueous solutions of alkaline carbonates, and is precipitated unchanged by addition of mineral acids. It is, however, gradually decomposed in an alkaline solution, as may be seen from the following experiment: one-half gram potassium hydrate (theory 0.45) was dissolved in 5 grams water and 2 grams of the ether added; but it was finally found necessary to add 0.2 potassium hydrate more before all the oil dissolved. On standing several hours some oil separated from the solution. This, however, dissolved again on addition of a small amount of potassium hydrate. The solution was then acidified, the solution extracted with ether, and only one gram acet-malonic ether was recovered by fractionation *in vacuo*. This decomposition was not studied any further, but a corresponding experiment with acet-ethyl-malonic ethers makes it very probable that malonic and acetic acids or ethers are formed.[1] The sodium derivative was made by dissolving 0.35 gram sodium in 5 grams absolute alcohol and adding 3 grams ether. The solutions heated when mixed, and soon solidified to a mass of white prismatic plates, which are very soluble in water, pretty soluble in alcohol and sparingly in ether. It is also but slightly soluble in concentrated caustic potash, and may therefore be obtained by adding acet-malonic ether to such a solution.

[1] Conrad and Brückner (Ztschr. phys. Chem. **7**, 290), in remarking on the saponification of malonic ether by sodium ethylate, state that these results are directly contrary to their own, but I fail to see that they are justified in such a conclusion. Acet-malonic ether acts as a well-marked acid substance, and it is not in the least surprising that its sodium derivative shows considerable stability. However, in mentioning that the ether dissolves unchanged in alkalies, I had no intention of asserting that the amount precipitated on adding acid is exactly that originally taken, but I am sure if it is decomposed at all it is only to a very slight extent. I do not feel at all certain whether these chemists have the same compound in view, as they still think that the neutral carb-ethoxyl-acet-acetic ether is acet-malonic ether, to judge from what they state in another part of their paper (page 284).

0.4610 gram vacuum-dried salt, which did not change in weight at 100°, gave 0.1492 gram Na_2SO_4.

	Theory for $CH_3-\dot{C}ONa-\dot{C}(COOC_2H_5)_2$.	Found.
Na	10.27	10.48

The presence of carbonyl was proven in acetyl-malonic ether by the formation of a phenylhydrazine derivative. Three grams ether were added to an aqueous solution containing equal weights of phenylhydrazine chlorhydrate and sodium acetate, and sufficient alcohol to effect solution was added. After standing a day, water was added to the solution, when a yellow crystalline precipitate fromed, which was purified by crystallising from alcohol, and an analysis gave the following result:

0.2449 gram substance gave 21 cc. nitrogen, $t = 14°$, $B = 766$ mm.

	Calculated for $CH_3-\overset{N_2HC_6H_5}{\overset{\vert}{C}}-CH(COOC_2H_5)_2$.	Found.
N	9.58	10.17

The hydrazone or hydrazo-derivative crystallises as white prismatic plates which are insoluble in cold water, pretty soluble in cold, easily in hot alcohol, and melt at 119°–121°.[1]

An alcoholic solution of hydroxylamine also acts on acetyl-malonic ether, forming a thick oil, but, as it could not be purified by fractionation, even *in vacuo*, it was not further examined.

The higher-boiling product formed in the action of acetyl chloride on sodium malonic ether gave the following figures on analysis:

0.1698 gram substance, burnt with $PbCrO_4$, gave 0.3363 gram CO_2 and 0.0994 gram H_2O.

0.2158 gram substance, burnt with $PbCrO_4$, gave 0.4284 gram CO_2 and 0.1305 gram H_2O.

	Theory for $(CH_3CO)_2=C=(COOC_2H_5)_2$.	Found. I.	Found. II.
C	54.09	54.01	54.16
H	6.56	6.51	6.72

Diacet-malonic ether decomposes when boiled under ordinary pressure, which is the reason its formation was overlooked by Lange, but it can be distilled with but slight decomposition *in vacuo*,

[1] Free phenylhydrazine appears to act differently. An ethereal solution deposited some crystals which are probably acetyl-phenyl-hydrazide, and the solution gave an oil that gradually solidified, but this substance is not identical with that above described. I shall examine this reaction more carefully.

boiling at 156° under 17 mm. pressure (oil-bath 185°). It behaves as a neutral oil towards caustic alkalies, only dissolving in them with decomposition on standing.

Free phenylhydrazine acts readily on the ether, forming β-acetyl-phenyl-hydrazide. To a solution of 1.4 grams substance in 6 grams dry ether, 2.1 grams phenylhydrazine (2 mols.) were added and the mixture cooled in ice. After a few minutes a crystalline substance was deposited, which increased on standing, and which was filtered after two days. This precipitate was crystallised several times from alcohol and formed flat prisms with obliquely truncated end-faces that began to soften at 127° and melted at 127.5°–128°. These are properties that agree with those given by Fischer[1] for β-acetyl-phenyl-hydrazide, and the following analysis confirms the formation of that body:[2]

0.1526 gram substance, dried at 100°, gave 0.3826 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_6H_5-NH-NHCOCH_3$.	Found.
C	64.00	64.18
H	6.66	6.98

Action of Chlorcarbonic Ether on Sodium Malonic Ether.

Conrad and Guthzeit[3] described methin-tricarbonic ether, which they obtained by the action of chlorcarbonic ether on sodium malonic ether in presence of benzene, as a neutral substance, not capable of forming a sodium derivative. As such properties are not in accordance with those indicated by the constitution of methin-tricarbonic ether it seemed of interest to prepare and re-examine the substance.

To 8.7 grams granulated sodium, under 300 grams dry ether, 60 grams malonic ether were added and, after no more hydrogen was given off, 40.4 chlorcarbonic ether gradually allowed to drop into the mixture. A reaction took place immediately, but it was not as energetic as in the corresponding experiment with sodium acet-

[1] Ann. Chem. (Liebig) **190**, 130.

[2] Although the constitution $(CH_3CO)_2=C=(COOC_2H_5)_2$ for diacetyl-malonic ether is probable, there is as yet no strict proof for it, as the compound may be $CH_3-CO(OCC_2H_3)-C=(COOC_2H_5)_2$, which should be a neutral body and also give acetyl-phenyl-hydrazide with phenylhydrazine. This applies to diacet- and dibenzoyl-acet-acetic ethers, and I shall examine the behavior of these substances towards the phenylhydrazine acetate solution, as it will be shown further on that this reagent gives a hydrazone with compounds from which free phenyl-hydrazine splits off acetyl, forming acetyl-phenyl-hydrazide.

[3] Ann. Chem. (Liebig) **214**, 31.

acetic ether. After standing twelve hours the odor of chlorcarbonic ether was no longer noticeable, and the solution was heated for an hour with an inverted cooler, after cooling extracted with water and the ether solution dried over sodium sulphate. On fractionation *in vacuo* of the oil remaining when the ether was distilled off, besides malonic and methin-tricarbonic ethers no other product could be isolated. The compound boils unchanged at 137°–138° (17 mm. pressure, bath 160°), solidifying on cooling in large crystals melting at 28°, and agrees in all its physical properties with the compound described by Conrad and Guthzeit. In its chemical behavior, however, I found a very marked difference, since, instead of being neutral towards aqueous alkalies it dissolved readily in them, even in aqueous sodium carbonate, and was precipitated again by the addition of a mineral acid. Instead of decomposing easily on contact with sodium ethylate it formed at once a sodium derivative. 0.5 gram sodium was dissolved in 5 grams absolute alcohol and 5 grams ether, dissolved in an equal weight alcohol, added while cooling, when the liquid soon solidified to a mass of white crystals. After standing several hours the precipitate was filtered out, washed with dry ether and dried *in vacuo*. The sodium derivative is readily soluble in water, and mineral acids precipitate methin-tricarbonic ether from this solution. The sodium estimations of this substance gave the following results:

0.3838 gram sodium compound dried *in vacuo* gave 0.1078 gram Na_2SO_4.

0.3671 gram sodium compound dried *in vacuo* gave 0.1025 gram Na_2SO_4.

	Theory for $C\begin{cases}(COOC_2H_5)_2\\OC_2H_5\\ONa\end{cases}$.	Found. I.	II.
Na	9.09	9.12	9.04

In view of the differences between the observations of Conrad and Guthzeit and my own on this product, it seemed hardly possible that we could have obtained the same compound, and I therefore prepared methin-tricarbonic ether according to their directions, by allowing chlorcarbonic ether to act on dry sodium malonic ether suspended in benzene. To 40.8 grams sodium malonic ether, prepared by adding the calculated amount of dry and finely powdered sodium ethylate to malonic ether while cooling, mixing well with a pestle, and drying *in*

vacuo to constant weight, 100 grams dry benzene and then gradually 24.4 grams chlorcarbonic ether, diluted with three times its volume of benzene, were added. The mixture was then heated three hours, when the reaction was completed, and after the usual operations the product distilled in a vacuum. From this experiment 10 grams almost pure malonic ether, about two grams of oil boiling between 110°–135° and 23 grams methin-tricarbonic ether were obtained. This ether agreed in all respects, both in its chemical and physical properties, with the product already described, and as I also obtained the same compound by the action of chlorcarbonic ether on a cold alcoholic solution of sodium malonic ether, no other explanation remains for the anomalous properties which Conrad and Guthzeit ascribe to methin-tricarbonic ether than that their observations regarding its neutrality and the non-formation of a sodium derivative were not correct.

An attempt was made to introduce ethyl into methin-tricarbonic ether according to the Conrad-Limpach method. The alcoholic solution remained strongly alkaline, even after standing ten hours, and it was then heated to 100°, when it gradually became neutral. The product, worked up in the usual manner, was distilled *in vacuo*, and yielded an oil which boiled at from 202°–204° under ordinary pressure. This consisted of ethyl-malonic ether. It seemed of interest to determine whether potassium malonic ether would also give solely methin-tricarbonic ether. 2.45 grams granulated potassium were brought under 40 grams dry ether and 10 grams malonic ether added gradually. A violent reaction took place with formation of the potassium derivative, but even after standing ten hours and shaking it was found impossible to convert all the malonic ether into its potassium compound, as only 600 cc. hydrogen were given off, instead of 700 cc., which should be formed from the amount of potassium taken. To this mixture 6.7 grams chlorcarbonic ether, diluted with twice its volume dry ether, were slowly added, and the product after standing 10 hours showed a neutral reaction and was worked up as described above. By fractional distillation *in vacuo* unchanged malonic ether and methin-tricarbonic ether were isolated; the latter compound dissolved completely in dilute caustic potash, and, in fact, the formation of a neutral compound other than malonic ether could not be detected.

Behavior of Carbon Dioxide towards Sodium Malonic and Acet-acetic Ethers.

According to a preliminary note,[1] carbon dioxide acts on sodium malonic ether, in alcoholic solution, with formation of the compound $CH\begin{smallmatrix}/\,COONa\\ \backslash\,(COOC_2H_5)_2\end{smallmatrix}$, which decomposes in contact with water into malonic ether and sodium bicarbonate. Such a compound may have the constitution $CH<\begin{smallmatrix}COOC_2H_5\\ C<\begin{smallmatrix}OCOONa,\\ OC_2H_5\end{smallmatrix}\end{smallmatrix}$ which would explain the facility with which it is decomposed by water. In order to prove which of these two structures is correct I wished to replace the sodium by ethyl and compare the compound thus obtained with methin-tricarbonic ether; but, although the conditions were varied, I have not been able to repeat my original experiments with the same result. On passing carefully dried carbon dioxide into an absolute alcoholic solution of sodium malonic ether while cooling, the formation of a white precipitate occurred, but this precipitate, in my later experiments, always consisted of sodium ethyl-carbonate and dissolved perfectly in water, while previously the precipitate gave malonic ether, although it had been washed with alcohol and dried well between layers of filter-paper. It would seem as if under certain conditions, which I have not been able to ascertain, the described compound is formed, while under other, probably the usual ones, the carbon dioxide dissolving in alcohol forms unstable $CO<\begin{smallmatrix}OC_2H_5\\ OH\end{smallmatrix}$, which acts on sodium malonic ether, setting free malonic ether and forming sodium ethyl-carbonate.

As the presence of alcohol interfered, some experiments on the action of carbon dioxide on sodium malonic ether suspended in ether were made. The sodium malonic ether was prepared by the action of granulated sodium on malonic ether dissolved in 15 times its volume of ether, care being taken to exclude water as far as possible, and through the thick mass, well cooled off in ice, carbon dioxide, dried first with sulphuric acid and then over phosphoric anhydride, was passed. It was noticed that the carbon dioxide was almost completely absorbed at first, and at the same time the sodium malonic ether began to go into solu-

[1] This Journal **9**, 126.

tion. After passing a slow current of carbon dioxide about an hour a clear solution was obtained, when the gas went through unabsorbed. This solution, on standing in a closed vessel, deposits a very little of a gelatinous substance, but the quantity was too small to permit an examination. The ethereal solution was examined as to its behavior towards water, ethyl iodide and chlorcarbonic ether. When extracted with water sodium carbonate goes into solution, and from the ether solution malonic ether was separated by fractionation *in vacuo*. To another portion a slight excess of ethyl iodide was added and the mixture allowed to stand at ordinary temperature for a week. The ether solution still showed a decided alkaline reaction, although the formation of considerable sodium iodide showed that a reaction had taken place, and it was then heated some hours at 50°. After the usual treatment and fractionation *in vacuo* malonic and ethyl-malonic ethers were isolated. A third portion was treated with chlorcarbonic ether, and after the reaction was completed malonic and methin-tricarbonic ethers were isolated from the liquid. From these results it would seem that there was still some unchanged sodium malonic ether in the ethereal solution, but that a part of the sodium derivative had undergone some change appears almost beyond question, as the solubility of carbon dioxide in ether is too small to cause the very considerable amount of sodium malonic ether to dissolve, and, besides, a very considerable amount of the gas had itself dissolved. It certainly seems as if carbon dioxide acts on sodium malonic ether to form an unstable sodium compound which is quite soluble in ether, a fact which precludes the formation of ethyl-sodium carbonate in the reaction, as this does not dissolve easily in ether. The compound evidently decomposes readily, since the ethereal solution evaporated *in vacuo* leaves a solid substance which is quite insoluble in ether. I shall continue the examination of this peculiar reaction, and hope my further work will throw more light on it.

That carbon dioxide really acts on sodium malonic ether in presence of ether is further confirmed by its behavior towards sodium acet-acetic ether under exactly the same conditions. In this case there is no absorption of the gas, and, no matter how long it is passed through the mixture, the sodium acet-acetic ether does not dissolve nor is it changed.

Action of Acetyl Chloride on Sodium Ethyl-malonic Ether.

To 5.7 grams granulated sodium under 100 grams dry ether 46 grams ethyl-malonic ether—a product boiling between 205°–206° was fractionated *in vacuo*, when it boiled at 104°–105° under 20 mm. pressure—were gradually added. Before quite all the ether was added a white precipitate of the sodium derivative began to separate, but the greater part of the sodium was already in solution. The mixture was allowed to stand at ordinary temperature for some hours and repeatedly shaken. After the evolution of hydrogen had entirely ceased, the flask was cooled in ice-water and 19.5 grams acetyl chloride slowly added, while shaking the flask. The precipitate of sodium ethyl-malonic ether dissolved after a small quantity of acetyl chloride had been added. After standing ten hours in ice-water the liquid had become yellowish and showed a very slight acid reaction. It was then shaken out with water (the use of alkalies must be avoided, as the compound formed is decomposed even in ethereal solution by contact with aqueous alkalies), the ether solution dried over sodium sulphate and heated in a water-bath until no more ether went off. The residue was then fractionated *in vacuo*, an operation which was repeated ten times, as a considerable quantity of the acet-ethyl-malonic ether goes over in the first fractionations above the correct boiling-point. From this experiment 19 grams of an oil boiling unchanged at 137°–137½° under 20 mm. pressure, 4 grams of the same product boiling at 136°–138° (20 mm.), about 4 grams of a liquid that went over 115°–118° which has not been further examined, some unchanged ethyl-malonic ether and a small quantity of a higher-boiling product—between 150°–160° at 20 mm.—but not in sufficient amount to purify by further fractionation, were obtained. Acetic acid was also found in the original aqueous extract. The principal product of the reaction was analysed with the following results:

0.1648 gram substance, burnt with $PbCrO_4$, gave 0.3458 CO_2 and 0.1173 H_2O.

0.1581 gram substance, burnt with $PbCrO_4$, gave 0.3320 CO_2 and 0.1035 H_2O.

	Theory for $CH_3—CO—C(C_2H_5)(COOC_2H_5)_2$.	Found. I.	II.
C	57.37	57.23	57.32
H	7.82	7.91	7.98

Acet-ethyl-malonic ether forms a colorless oil which boils at 137°–137½° under 20 mm. pressure (bath 165°), and is sparingly soluble in water, readily in alcohol and ether. It behaves towards alkalies as a neutral body, a property in accordance with its constitution, but undergoes, even with aqueous alkalies, a decomposition very easily, to form an acetate and an ethyl-malonate. This reaction may also be effected by continued shaking of an ethereal solution of the compound with aqueous potash, when it is gradually completely decomposed, and the alkaline solution then contains potassium acetate and ethyl-malonate, while the ethereal solution contains a very considerable amount of ethyl-malonic ether. On adding the calculated quantity of sodium ethylate (dried at 200° in hydrogen) to acet-ethyl-malonic ether cooled off in ice, a reaction took place immediately, and the ethylate dissolved in the ether to form an amber-colored liquid, which smelt strongly of acetic ether. The mixture stood in the cold a day and was then dissolved in cold water and extracted with ether. After drying over sodium sulphate the ethereal solution was fractionated, and not far from the calculated quantity of ethyl-malonic ether, besides some acetic ether, was isolated. The aqueous solution gave off no carbon dioxide on acidulating, and contained some acetic and ethyl-malonic acids:

$$CH_3{-}CO{-}\overset{\displaystyle C_2H_5}{\overset{|}{C}}(COOC_2H_5)_2 + NaOC_2H_5 =$$

$$CH_3{-}COOC_2H_5 + C\begin{cases} COOC_2H_5 \\ ONa. \\ OC_2H_5 \end{cases}$$

Free phenylhydrazine acts readily on the body, forming acet-phenyl-hydrazide. 4 grams substance were dissolved in 3 grams dry ether, and 1.9 grams phenylhydrazine added to the solution. No heat was perceptible, nor was any water formed in the reaction, but in about an hour long crystals began to separate, which increased in number until the solution appeared almost solid. After standing 36 hours the crystals were filtered, washed with a little ether, and weighed 2.3 grams after drying in the air. The crude product melted at 123°–125°, but after several crystallisations from alcohol the melting-point remained constant at 127.5°–128.5°.

The substance has all the properties noted by Fischer[1] for the compound $C_6H_5—NH—NH—CO—CH_3$, the formation of which was confirmed by the following analysis:

0.1317 gram substance gave 0.3100 gram CO_2 and 0.0827 gram H_2O.

	Calculated for $C_6H_5—NH—NHCOCH_3$.	Found.
C	64.00	64.15
H	6.66	6.97

On evaporation of the ethereal filtrate an oil was obtained that gave a few more crystals of the hydrazide on standing in a vacuum. It was not further examined, but probably consisted largely of ethyl-malonic ether, as the hydrazide obtained was almost in theoretical quantity; 2.3 grams were obtained instead of the 2.5 grams that should be formed if the reaction takes place according to the following equation:

$$CH_3—CO—\overset{\displaystyle C_2H_5}{\overset{|}{C}}=(COOC_2H_5)_2 + C_6H_5—NH—NH_2 =$$
$$C_2H_5—CH(COOC_2H_5)_2 + C_6H_5—NH—NH—CO—CH_3.$$

The facility with which acet-phenyl-hydrazide is formed appears indeed surprising in view of the ease with which these ketone-acid ethers form hydrazones with that reagent, but it is evidently a result of the loosening of the affinity of carbon to carbon by the accumulation of negative radicles on one carbon. It was of importance to bring a decided proof that acetyl in this compound is joined to carbon, as all the decompositions hitherto described accord also with the properties of an acetyl derivative in which it is joined to oxygen. That this is not the case, however, was shown by the preparation of the hydrazone of acet-ethyl-malonic ether. To 2 grams each of phenylhydrazine chlorhydrate and sodium acetate dissolved in 16 grams water, 2 grams of the compound and sufficient alcohol (20 grams) were added to form a clear solution, even when it was cooled to 0°. After several hours an oil began to separate, which increased in volume on longer standing, and was separated from the mother-liquor. It was dissolved in alcohol, precipitated by addition of water, this operation repeated and, after the mother-liquor was removed, the oil dissolved in ether, dried over sodium sulphate, filtered, and evaporated *in vacuo*. After

[1] Ann. Chem. (Liebig) **190**, 129.

standing several days the liquid had turned almost solid, and it was then pressed between filter-paper and washed a number of times with petroleum ether. As I found it impossible to recrystallise this substance, it was dried *in vacuo* and gave the following results for nitrogen:

0.1269 gram substance gave 10.2 cc. N at 13° and 759 mm. pressure.

0.2618 gram substance gave 19.8 cc. N at 15° and 756 mm. pressure.

	Theory for $CH_3-\overset{N_2HC_2H_5}{\overset{\|\|}{C}}-\underset{C_2H_5}{\overset{\|}{C}}=(COOC_2H_5)_2$.	Found. I.	II.
N	8.75	9.49	9.17

The hydrazone forms slightly yellowish, large prisms that melt at 44°–45°, and are soluble in the usual solvents with the exception of ligroin and petroleum ether. If allowed to stand in a desiccator over sulphuric acid it gradually turns into an oil, undergoing some chemical change, as it was found impossible to reconvert this oil into the solid substance.

Action of Chlorcarbonic Ether on Sodium Ethyl-acet-acetic Ether.

The ethyl-acet-acetic ether used in these experiments was made according to the Conrad-Limpach method and fractionated under ordinary pressure. This product was then extracted twice with dilute caustic potash to free it from a little acet-acetic ether which it is difficult to remove by fractionation, and the product then distilled twice *in vacuo*. It boils at 95° under 20 mm. pressure (bath 115°) without decomposition. To 8.2 grams granulated sodium under 125 grams dry ether 55.5 ethyl-acet-acetic ether were added from a drop-funnel, the mixture being kept cool in ice-water. When most of the ether had been added the contents of the flask turned thick, owing to the separation of the sodium derivative. The flask was removed from ice-water, repeatedly shaken and, when no more hydrogen was given off, again cooled off in ice and 38.5 chlorcarbonic ether added in small portions, while shaking the flask. The sodium derivative went into solution after a few grams of chlorcarbonic ether had dropped in, and the solution remained clear until the greater part of this reagent was added, when it began to take a gelatinous consistency. A

test for sodium chloride at this point showed that a considerable proportion of the chlorcarbonic ether must have reacted with the sodium derivative. The mixture stood several hours in ice, then over night at ordinary temperature, but still showed an alkaline reaction, which did not disappear even on standing a day longer. It was then heated gently for a half-hour (after which it gave only a very faint alkaline reaction) and extracted twice with water. The solution was dried over sodium sulphate and, after removal of the ether, fractionated *in vacuo*. Besides some ethyl-acet-acetic ether there was only one other product formed. It was much easier to obtain this pure than the product in the corresponding experiment with sodium ethyl-malonic ether, and it was also obtained in a much larger yield. The above experiment gave 45 grams of oil boiling from 146° to 148° under 20 mm., 6 grams from 120° to 143°, but the thermometer did not stop at 138° and there was no indication of the formation of acet-ethyl-malonic ether; 3 grams from 143° to 146° and 8 grams from 148° to 152°, which undoubtedly consisted principally of the new body. After several fractionations in a vacuum a constant-boiling product was obtained, which was analysed with the following results:

0.1547 gram oil, *burnt in open tube*, gave 0.3219 gram CO_2 and 0.1118 gram H_2O.

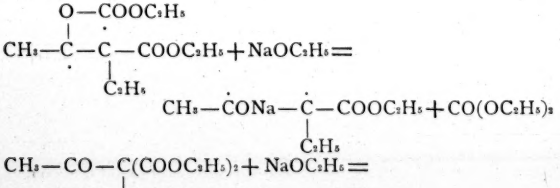
0.1449 gram oil, burnt with $PbCrO_4$, gave 0.3060 gram CO_2 and 0.1040 gram H_2O.

	Theory for $CH_3-\underset{\displaystyle C_2H_5}{\overset{\displaystyle OCOOC_2H_5}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}-COOC_2H_5$.	Found. I.	Found. II.
C	57.37	56.74	57.58
H	7.82	8.03	7.97

Carb-ethoxyl-ethyl-acet-acetic ether is a colorless oil that boils at 146° under 20 mm. pressure (bath 175°) with very slight decomposition, and is sparingly soluble in water, miscible with ether and alcohol. It acts as a neutral body towards aqueous solutions of alkaline carbonates and alkalies, but gradually undergoes decomposition in contact with them. The substance differs not only in its boiling-point from acet-ethyl-malonic ether, but also very characteristically in its behavior towards phenylhydrazine and sodium ethylate. To 6.8 grams substance, cooled in ice, 2 grams powdered sodium ethylate (which contained a little alcohol) were added, while stirring the mixture. A violent reaction took place, and, unless the flask was well cooled off, the contents of the flask

became quite warm. After standing a few minutes a semi-solid, slightly yellow mass was formed and the decomposition was virtually completed. The mixture stood a day in a cool place and was then extracted with water. There was no odor of acetic ether noticeable, which was so marked in the corresponding experiment with acet-ethyl-malonic ether. After extracting with ether, drying the extract and fractionating, a small quantity of a liquid boiling at 125°–135° went over, when the thermometer rose very rapidly to 192°, and from that temperature to 198° three grams of ethyl-acet-acetic ether distilled off. The oil was shown to be ethyl-acet-acetic ether by conversion into a pyrazolone, according to a new method which I shall describe farther on. The portion boiling between 125°–135° contained a small quantity of carbonic ether, as, after treating it with alkalies and acidulating, carbon dioxide was given off, although the amount of carbonic ether formed was less than was obtained in decomposing carb-ethoxyl-acet-acetic ether. Above 198° a very small quantity of oil remained that did not pass over even when the metal bath was heated to 260°. This probably consisted of unchanged substance. The aqueous solution after extraction with ether, on addition of dilute sulphuric acid, gave off a very considerable quantity of carbon dioxide, and, on extracting with ether, a small quantity of propyl-methyl-ketone was obtained, evidently formed in the decomposition of ethyl-acet-acetic ether by the alkali.

Carb-ethoxyl-ethyl-acet-acetic ether, therefore, gives mainly ethyl-acet-acetic ether, carbon dioxide and carbonic ether when treated with sodium ethylate, while the isomeric acet-ethyl-malonic ether yields acetic acid and ethyl-malonic and acetic ethers:



Quite as marked is the difference in the behavior of the isomers towards phenylhydrazine. Carb-ethoxyl-ethyl-acet-acetic ether was treated, under exactly the same conditions as already described with acet-ethyl-malonic ether, but in this experiment there was no crystalline deposit, even when the mixture stood several weeks. On evaporating the ether *in vacuo* and allowing the residue to remain there for some days it partially solidified, but did not become altogether solid, even on long standing. The product was filtered under pressure and the almost solid mass washed with carbon disulphide, in which the liquid dissolves, leaving a yellowish crystalline substance which was obtained pure by four crystallisations from that solvent. The substance melted at 81° and was in every respect identical with the product obtained by the action of phenylhydrazine on carb-ethoxyl-acet-acetic ether, a conclusion which was confirmed by the following estimation:

0.1237 gram substance gave 16.8 cc. N at 14° and 747 pressure.

	Theory for $C_6H_5N_2HCOOC_2H_5$.	Found.
N	15.55	15.79

The mother-liquor from the hydrazide was not further examined, but very probably contained some ethyl-acet-acetic ether and products formed by the action of phenylhydrazine on that compound. It may be mentioned that the amount of the hydrazide obtained is comparatively small for the quantity of substance used.

Preparation and Properties of Acet-methyl-malonic and Carb-ethoxyl-methyl-acet-acetic Ethers.

Although the above-described experiments with sodium acet-acetic and malonic ethers and their ethyl homologues make it very probable that the corresponding methyl derivatives are analogous compounds, it seemed of sufficient interest to make these experiments. In reactions depending on the relative negativity and positivity of the unsaturated carbons whether an addition or substitution takes place, any change in this relation may give rise to a somewhat different result; and, even though analogous results were obtained, these would be but desirable confirmations, as the synthesis of derivatives of acet-acetic ether in which the introduced radicle is joined to oxygen and not to carbon is certainly very anomalous.

The methyl-malonic ether used in the following experiment was prepared by quickly adding methyl iodide to sodium malonic ether kept cool in ice-water, and fractionating the product *in vacuo*. It was thought possible to avoid in this way the formation of methyl or mixed malonic ethers,[1] which are always formed in small quantity under the usual conditions, but, even after repeated fractionation of a product boiling perfectly constantly at 95.5° (corrected) under 20 mm. (bath 125°), the density determination of the product was $D = 1.028\,\frac{15^\circ}{15^\circ}$, showing that it is not possible to obtain a perfectly pure product according to the Conrad-Limpach method.

The ether was converted into the sodium derivative by treating with granulated sodium in ethereal solution—a reaction which is more difficult to complete than that with ethyl-malonic ether, as the sodium derivative is somewhat less soluble in ether—the mixture cooled in ice, and the required amount of acetyl chloride added. The further treatment was like that described with the ethyl derivative, and by repeated fractionating *in vacuo* a pure product was isolated and analysed.

0.1860 gram substance, burned with $PbCrO_4$, gave 0.3792 gram CO_2 and 0.1300 gram H_2O.

	Theory for $CH_3-CO-\overset{CH_3}{\overset{\vert}{C}}(COOC_2H_5)_2$.	Found.
C	55.55	55.59
H	7.40	7.80

Besides this compound, the only products that could be isolated were acetic acid and unchanged methyl-malonic ether. Acet-methyl-malonic ether boils without decomposition at 129.5°–130° (corrected, 131°–131.5°) under 20 mm. pressure (bath 160°), and is sparingly soluble in water, miscible with alcohol and ether. Like the ethyl compound it behaves as a neutral body towards alkalies, but is gradually decomposed by them. Dry sodium ethylate acted very readily on the ether in the cold, forming when first added white fumes, and soon a strong odor of acetic ether became noticeable. After standing some hours in ice-water the contents of the flask were treated with water, then acidulated and extracted with ether. From the ether-extract acetic acid and ethyl and methyl-malonic ethers were isolated by frac-

[1] Perkin: J. Chem. Soc. **45**, 510.

tionation. A solution of one part acet-methyl-malonic ether in two parts dry ether and the equivalent quantity of phenyl-hydrazine soon deposits crystals, which increase in number on longer standing. These crystals were obtained pure by crystallising several times from alcohol, and melted at 127.5°–128.5°. All their properties agree with those of β-acet-phenyl-hydrazide, the formation of which was confirmed by a nitrogen estimation:

0.1196 gram substance gave 19 cc. N at 4.5° and 741 mm. pressure.

	Theory for $C_6H_5-NH-NH-CO-CH_3$.	Found.
N	18.6	19.0

With phenylhydrazine acetate solution a different product, probably a hydrazone, is formed, but the reaction was not further examined.

To prepare carb-ethoxyl-methyl-acet-acetic ether, chlorcarbonic ether was allowed to act on sodium methyl-acet-acetic ether in presence of ether, while cooling with ice, under the conditions already described with the ethyl derivative. By repeated fractionation *in vacuo* the product of the reaction was separated into comparatively little of an oil boiling at 120°–135°, which contained some carbonic ether, besides some unchanged methyl-acet-acetic ether, and about 50 per cent. of the theoretical quantity of the new ether, which was analysed with the following results:

0.2138 gram oil, burnt with $PbCrO_4$, gave 0.4360 gram CO_2 and 0.1521 gram H_2O.

	Theory for $CH_3-\dot{C}<\begin{matrix}OCOOC_2H_5\\ \dot{C}-COOC_2H_5\\ \dot{C}H_3\end{matrix}$.	Found.
C	55.55	55.63
H	7.40	7.85

Carb-ethoxyl-methyl-acet-acetic ether is a colorless oil, boiling at 136° (corrected, 137°) under 20 mm. (bath 160°). It is neutral in its behavior towards aqueous alkalies, but gradually undergoes decomposition when allowed to stand with such solutions.

Sodium ethylate (dried in hydrogen at 200°) acted readily on the ether cooled in ice, and white fumes formed in the flask. After thoroughly mixing and allowing the product to stand some hours it was worked up as already described, and considerable carbon dioxide, some carbonic ether and methyl-acet-acetic ether were obtained as decomposition-products:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle O-COOC_2H_5}{\overset{|}{C}}}-C-COOC_2H_5 + NaOC_2H_5 =$$

$$CH_3-CONa-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-COOC_2H_5 + CO(OC_2H_5)_2.$$[1]

Towards phenylhydrazine it behaves like the corresponding ethyl derivative, the hydrazide melting at 80° and a heavy oil being the products of the reaction, but no acet-phenylhydrazide was formed.

Properties of Propionyl-malonic Ether.

This compound was prepared according to Lange's[2] directions, by the action of propionyl chloride on sodium malonic ether in presence of ether, and also by first preparing the sodium malonic ether by the action of sodium ethylate on malonic ether, and after drying in a vacuum, treating a mixture of the substance and ether as before. In either case, however, it is well to cool in ice during the reaction, as a somewhat better result is thereby obtained. The yield is comparatively small, a considerable quantity of malonic ether and a high-boiling liquid, undoubtedly dipropionyl-malonic ether, which decomposed when distilled under ordinary pressure, were formed. The re-formation of malonic ether is undoubtedly due to the action of propio-malonic on sodium malonic ether, as the former has a much stronger acid character than malonic ether and it therefore substitutes hydrogen for sodium.

Propio-malonic ether, like acet-malonic ether, acts as an acid towards aqueous solutions of alkaline carbonates and alkalies, dissolving in them without noticeable decomposition, and is precipitated on acidulation. The sodium derivative was obtained by adding dry sodium ethylate to the ether, kept well cooled in ice,

[1] In these experiments with sodium ethylate, carbon dioxide was formed in larger quantities than carbonic ether. It is possible that ether is formed as a direct product of the reaction, as it has been shown to be formed when sodium ethylate acts on organic ethers (Lossen and Köhler, Ann. Chem. (Liebig) **263**, 207). In this case its formation would be represented as follows:

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OCOOC_2H_5}{\overset{|}{C}}}-C-COOC_2H_5 + NaOC_2H_5 = CH_3-CONa-\underset{\displaystyle CH_3}{\overset{|}{C}}-COOC_2H_5 + CO_2 + (C_2H_5)_2O,$$

or it may be formed secondarily by the action of sodium ethylate on carbonic ether:

$$CO(OC_2H_5)_2 + NaOC_2H_5 = CO<\overset{ONa}{OC_2H_5} + (C_2H_5)_2O.$$

[2] Ber. d. chem. Ges. **20**, 1326.

when it solidified to a crystalline mass. This was pressed between filter-papers, washed with a little dry ether, and dried *in vacuo*.

0.4173 gram substance gave 0.2224 gram Na_2SO_4.

	Calculated for $C_2H_5-\dot{C}ONa-\dot{C}-(COOC_2H_5)_2$.	Found.
Na	16.66	16.80

It dissolved readily in water to form a clear solution, and dilute sulphuric acid precipitated propio-malonic ether. If, however, the alkaline solution was allowed to stand, the ether gradually underwent decomposition.

Action of Phenylhydrazine on Sodium Acet-succinic Ether.

As phenylhydrazine acts readily on ethers of ketone acids forming hydrazones or hydrazo-products, it seemed of interest to ascertain whether their merotropic sodium derivatives would likewise give such compounds. Although the sodium derivatives do not contain a ketone-carbonyl, still hydrazones or hydrazo-products may be formed by addition of phenylhydrazine to the unsaturated carbons and subsequent elimination of sodium hydrate, a reaction which is represented by the following equations:

$$CH_3-\dot{C}ONa-CH-COOC_2H_5 + C_6H_5N_2H_3 =$$

$$CH_3-\underset{\displaystyle N_2H_3C_6H_5}{\overset{|}{C}}ONa-CH_2-COOC_2H_5 =$$

$$CH_3-\underset{\displaystyle N_2HC_6H_5}{\overset{|}{C}}-CH_2-COOC_2H_5 \text{ (or } CH_3-\underset{\displaystyle N_2H_3C_6H_5}{\overset{|}{C}}-CH-COOC_2H_5) + NaOH.$$

A few experiments in this direction have been made, beginning with acet-succinic ether, as its phenylhydrazine derivative had been obtained in a solid state and its sodium derivative is easily soluble in ether. The acet-succinic ether was prepared in the usual manner, but the crude product was distilled *in vacuo*, as I found with Gottstein[1] that it is impossible to obtain this compound pure by distillation under ordinary pressure. It passes over unchanged at 167°–168° under 35 mm. pressure (bath 195°).

10 grams of the ether were dissolved in 25 grams dry ether and 1.06 grams sodium added, of which all but a very small quantity finally went into solution. After removing the undissolved

[1] Ann. Chem. (Liebig) **216**, 36; also Perkin: J. Chem. Soc. **45**, 517.

sodium, 5 grams phenylhydrazine were added and the solution allowed to stand five days. Only a very slight deposit had separated, and the solvent was removed by evaporation *in vacuo*. The residue was extracted with water, separated from some insoluble oil, and the aqueous alkaline liquid acidulated with acetic acid, when a crystalline precipitate was deposited. This precipitate dissolved almost completely in boiling water, and was separated from a small amount of insoluble liquid. The yellowish crystals were purified by several crystallisations from alcohol.

0.1262 gram substance, dried at 100°, gave 0.2858 CO_2 and 0.0629 H_2O.

0.2257 gram substance, dried at 100°, gave 23.3 cc. N, $t = 13°$, $B = 764$ mm.

	Theory for $C_{13}H_{13}O_3N_3$.	Found. I.	II.
C	62.06	61.76	...
H	5.17	5.54	...
N	12.06	...	12.31

The new compound forms large white prisms that melt at 175°–177°, but begin to soften considerably below that temperature. They are sparingly soluble in hot ligroin, benzene and chloroform, somewhat more in cold water and hot chloroform, pretty easily soluble in hot water, alcohol and acetic ether. They are also soluble in caustic alkalies, and are precipitated unchanged by addition of acetic acid.

The sodium derivative formed in this reaction may be obtained by allowing phenylhydrazine to act on an absolute alcoholic solution of sodium acet-succinic ether, the substances being used in molecular proportions. If an excess of alcohol was avoided the solution solidified on standing to a mass of large prisms, which were filtered, washed with a very little absolute alcohol, then with ether and dried *in vacuo*.

0.3298 gram substance gave 0.095 gram Na_2SO_4.

	Calculated for $C_{13}H_{11}NaO_3N_2$.	Found.
Na	9.06	9.34

Heated to 100° it slowly decomposes, turning yellowish brown. It dissolves in water, and addition of acetic acid precipitates the substance melting at 173°–177°. The crude precipitate in the above experiment contained a second compound, which can be separated from it by extracting with water, in which it does not

dissolve. This substance melted at 80°, and was identical with the "hydrazone" obtained by Knorr,[1] by the action of phenylhydrazine on free acet-succinic ether. The amount formed is, however, small in comparison to that of the sodium derivative, of which as much as 80 per cent. of the theoretical yield was obtained. The formation of this "hydrazone" could not be observed when ethereal sodium acet-succinic ether was employed, and it may be due to the presence of a small quantity of free acet-succinic ether, even though there was sufficient sodium ethylate to complete the reaction.

The compound $C_{13}H_{11}NaO_3N_2$ is formed from a molecule of acet-succinic ether and one of phenylhydrazine by the abstraction of two molecules of alcohol. The reaction and the constitution of the substance are very likely correctly represented by the following equations:

$$CH_3-\dot{C}ONa-\dot{C}(CH_2-COOC_2H_5)-COOC_2H_5 + C_6H_5NH-NH_2 =$$

$$CH_3-\dot{C}ONa-\dot{C}<\begin{matrix}CH_2\\ \\ CH_2\end{matrix}>\begin{matrix}CO\\ \\ CO\end{matrix}>N-NHC_6H_5 + 2C_2H_5OH;$$

$$CH_3-\dot{C}ONa-\dot{C}<\begin{matrix}CH_2\\ \\ CH_2\end{matrix}>\begin{matrix}CO\\ \\ CO\end{matrix}>N-NHC_6H_5 + CH_3COOH =$$

$$CH_3-\dot{C}OH-\dot{C}<\begin{matrix}CH_2\\ \\ CH_2\end{matrix}>\begin{matrix}CO\\ \\ CO\end{matrix}>N-NHC_6H_5 =$$

$$(\text{or } CH_3-CO-CH<\begin{matrix}CH_2\\ \\ CH_2\end{matrix}>\begin{matrix}CO\\ \\ CO\end{matrix}>N-NHC_6H_5) + CH_3COONa.$$

Since phenylhydrazine reacts on free acet-succinic ether with great readiness even in the cold to form its "hydrazone," it certainly seems as if the formation of an entirely different product from sodium acet-succinic ether indicates different constitutions for the free ether and its sodium derivative, a fact which finds its best explanation in the merotropy of the two substances. It may appear, however, as if the sodium in sodium acet-succinic ether

[1] Ber. d. chem. Ges. **17**, 2151.

favored the formation of acet-succin-hydrazanil[1] instead of the "hydrazone," inasmuch as the latter substance has many less marked acid properties; but this explanation is not valid, as it will be shown further on that these "hydrazones" are unstable in presence of sodium ethylate or hydrate, they passing over into the corresponding pyrazolone, which class of compounds possess very decided acid properties and form stable sodium derivatives. A further confirmation of the above-stated view is found, I believe, in the behavior of sodium acet-succinic ether, in alcoholic solution, towards phenylhydrazine when the proportion of two molecules of the base to one of the sodium derivative is taken. Under these conditions a precipitate of the sodium acet-succin-hydrazanil appeared only after the solution had stood for some days, and, even after standing much longer, the quantity was not so great as when equal molecules were taken. This precipitate dissolved almost completely in water, and the solution gave acet-succin-hydrazanil on acidulating with acetic acid. The filtrate was evaporated in a vacuum, extracted with water (a small amount of solid did not dissolve, probably the "hydrazone") and gave an oil on acidulating with chlorhydric acid, which partially solidified on long standing, but the amount obtained did not permit further examination. I intend to repeat this experiment on a larger scale and examine it more thoroughly, although the formation of sodium acet-succin-hydrazanil in presence of an excess of phenylhydrazine is certainly strong evidence against the absence of a ketone-carbonyl in sodium acet-succinic ether. A number of experiments on the action of phenylhydrazine on the sodium derivatives of acet-acetic and ethyl-acet-acetic ethers have been made, but, as they are not completed, I shall return to this subject in a later paper.

A New Method of Converting Acet-acetic Ether and its Derivatives into Pyrazolones.

This interesting class of compounds was discovered by Knorr by heating the "hydrazones" of the ethers of β-ketone acids. The derivative of acet-acetic ether is converted with loss of alcohol at 100°, while its homologues require heating to a higher temperature. The above-described formation of phenyl-methyl-

[1] I should like to suggest this name of hydrazanil for the derivatives of phenylhydrazine corresponding to the anils.

pyrazolone in the action of phenylhydrazine acetate on carbethoxyl-acet-acetic ether in the cold induced me to make a similar experiment with acet-acetic ether, and here too the same pyrazolone was obtained. According to E. Fischer[1] the presence of a free mineral acid interferes with the formation of hydrazones with aldehydes and ketones, prevents it in the case of levulinic and acet-acetic acids, but not with α-carbonyl acids. It has already been shown[2] that in using levulinic ether, instead of the free acid, a hydrazone is readily obtained, and the same difference seemed probable between acet-acetic acid and its ether.

To a mixture of acet-acetic ether and phenylhydrazine chlorhydrate, the addition of three or four drops strong chlorhydric acid caused no apparent change, but when the flask was heated for a moment in a water-bath a reaction took place, the salt dissolving to form a clear solution, and alcohol and water vapors were given off. The time required to complete the reaction depends on the amount of the substance used, but ten or fifteen minutes' heating was generally sufficient. The contents of the flask were dissolved in water and carefully neutralised with dilute caustic soda, when an oil was precipitated which soon solidified. This substance after crystallising with alcohol melted at 127°, acted both as a base and an acid, and was identical with phenyl-methyl-pyrazolone obtained by Knorr on heating the "hydrazone" of acet-acetic ether at 100°. The yield obtained was almost the theoretical.

The same result was obtained by heating the sulphate of phenylhydrazine and several drops of sulphuric acid, or the hydriodate and hydriodic acid, with acet-acetic ether, although the crude pyrazolone formed in these reactions was not as pure as when chlorhydric acid was used. The formation of phenyl-methyl-pyrazolone proceeds, indeed, even in aqueous solution when chlorhydric, hydriodic or sulphuric acid is present. A solution of phenylhydrazine chlorhydrate in 8 parts water with a few drops of chlorhydric acid and acet-acetic ether, in molecular proportions, formed on shaking an emulsion, and the ether soon began to dissolve. After several hours, the time depending on the quantities used, a clear solution was formed, which now contained the chlorhydrate of phenyl-methyl-pyrazolone, as the careful neutralisation of the solution gave that substance in almost the theoretical amount.

[1] Ann. Chem. (Liebig) **236**, 146. [2] A. Michael: J. prakt. Chem. [2] **44**, 115.

The experiments on the pyrazolone formation by mineral acids have extended thus far to methyl, ethyl-acet-acetic and acet-succinic ethers, and with these ethers the results obtained were analogous to those just described for acet-acetic ether, with the exception that the chlorhydrate salts of the alkyl-acet-acetic ethers are less soluble in water. For instance, when ethyl-acet-acetic ether is treated with a slightly acid solution of phenyl-hydrazine chlorhydrate, it gradually disappears to make place for a crystalline substance, which melted at 140°–141°, and consisted of the chlorhydrate of phenyl-ethyl-methyl-pyrazolone. By dissolving these crystals in warm water and carefully neutralising with alkalies, the free pyrazolone, melting at 108°, was obtained.

The pyrazolone formation by mineral acids has been used in this research to prove the presence of acet-acetic ether and its homologues, and as only a fraction of a gram is necessary it will be found of use. This reaction may be of service to distinguish between true formyl and ketone-derivatives and those compounds which behave in a similar manner toward free phenylhydrazine, and it will be further studied from this point of view.

The above synthesis of phenyl-methyl-pyrazolone implies the intermediate formation of the "hydrazone," which evidently is unstable in the presence of a mineral acid. To test this view the "hydrazone" was prepared and found to be a solid and not a liquid as described by Knorr. This observation has been recently published by Nef,[1] and I should not mention my results, if they did not differ somewhat from those stated by him. Nef allowed phenylhydrazine to react with acet-acetic ether, added calcium chloride to accelerate the reaction, then extracted the ether solution with dilute sodium hydrate and finally with dilute sulphuric acid. The addition of calcium chloride is unnecessary, as the substances act with great readiness, even under 0°, and give the required amount of water. Extracting with sodium hydrate is also undesirable, as there is no unchanged acet-acetic ether, as Nef assumed, and neutralising the alkaline solution only precipitates phenyl-methyl-pyrazolone. The same remark applies equally to the extraction with dilute sulphuric acid obviously to remove unchanged hydrazine, but by neutralising the extract only pyrazolone is obtained. It will be shown further on that these operations only entail a loss of "hydrazone."

[1] Ann. Chem. (Liebig) **266**, 71.

In my experiments the theoretical quantities of hydrazine, acet-acetic ether and two parts of dry ether were mixed, the solution being cooled in ice, and the mixture allowed to stand for some hours. The water formed in the reaction was removed and the ether solution dried over sodium sulphate. On allowing this solution to evaporate *in vacuo* it gradually solidified to a crystalline mass, which was free from the oil that Nef obtained with his crude product. The product was somewhat yellowish and may be partially purified by extracting with petroleum ether; a pure substance was obtained by dissolving it in a little ether and precipitating by addition of petroleum ether, when it separated as large colorless prisms that began to fall together at about 46° and melted at 50°–51°. According to Nef the solid substance cannot be kept unchanged longer than two days, but the above product underwent no change until after standing several weeks, when it gradually began to turn yellowish, and even after standing for months, it had not turned into an oil, as Nef observed with his substance, but was still almost solid.[1]

In another respect I found a very notable difference between Nef's and my observations, as he claims his product can be heated for a long time at 100° without change, and only passed over into the pyrazolone when heated to 200° in a vacuum. As Knorr showed that the pyrazolone may be prepared by heating his oil to 100°, such a divergence in the stability towards heat would seem to indicate a chemical difference in the solid and liquid "hydrazones." I found on trying the experiment with the solid "hydrazone" that after heating it for a short time at 100° the formation of alcohol began to take place, and that, on sufficiently long heating at that temperature, the liquid turned completely solid and then consisted of phenyl-methyl-pyrazolone.[2]

The "hydrazone" is converted both by mineral acids and by alkalies with the greatest readiness into its pyrazolone. Treated in the cold with dilute chlorhydric or sulphuric acid, it soon went into solution, which then contained the corresponding salt of phenyl-methyl-pyrazolone. The decomposition is about quantitative, and the pyrazolone is obtained almost pure by neutralising the solu-

[1] It is not improbable that Nef's product was not perfectly pure, as his carbon estimation is very low.

[2] The solid "hydrazone" was subsequently prepared according to Nef's directions and the product converted by heating at 100° into the pyrazolone. I am at a loss to explain such experimental differences, but it would be certainly of interest if Nef would repeat his experiment.

tion carefully with alkalies. A similar result is obtained when the molecular quantity of an alcoholic solution of an alkali is added to the "hydrazone," or when the alkali, in the form of fine powder, is added to a solution of the "hydrazone" in alcohol. The solution turns yellowish, and after several minutes the compound has passed over into the sodium derivative of phenyl-methyl-pyrazolone. This pyrazolone-formation is evidently connected with the decided basic and acid properties of the substance. We have in these reactions good illustrations of that tendency to neutrality which plays so prominent a function in organic chemistry.

The above result induced me to re-examine the behavior of aldehydes and ketones towards phenylhydrazine chlorhydrate, and it was found that Fischer's observation[1] regarding the prevention or retarding of hydrazone formation by mineral acids only applies to ketones and not to the aldehydes of monobasic acids. On adding fatty aldehydes to a solution of phenylhydrazine chlorhydrate in water, even when some free acid is present, there is an immediate reaction with the formation of liquid hydrazones, like those Fischer obtained by using the acetate solution. Aromatic aldehydes behave in a similar manner, except that solid hydrazones are formed, that agree in their melting-points with those already described by Fischer.

The retardation is, however, very decided in the case of fatty and aromatic ketones, which act immediately when the acetate mixture is used, but with the chlorhydrate solution gradually only after long standing, although finally the same products are formed. This difference in the behavior of ketones and aldehydes towards phenylhydrazine chlorhydrate is of interest, as it may be used to distinguish between an aldehyde and ketone, and probably also as a means of separating them.

Remarks on J. U. Nef's Paper, "Zur Kenntniss des Acetessigäthers."[2]

A number of the experimental errors to be found in this contribution to our knowledge of the constitution of acet-acetic ether have already been noticed in the preceding pages, and as several other statements made in it seem to support the views peculiar to Nef, the work upon which they are based has been carefully repeated and they, too, have been found inaccurate. It is quite

[1] Ber. d. chem. Ges. **17**, 573. [2] Ann. Chem. (Liebig) **266**, 52.

beyond the scope of these remarks to call attention to more than a few of the many mistakes and misconceptions that occur in Nef's paper.

In my paper on the constitution of sodium acet-acetic ether I called attention to the strong negative character of its carbonyl-oxygen, and expressed the opinion that the sodium derivative probably consists of a mixture of two compounds,[1] both of which would give the same products with alkyl iodides, but different compounds with alkylene iodides. A number of pages before stating this opinion for the first time[2] I remarked on the different behavior of sodium malonic ether, according to the manner in which it is prepared, and also stated that sodium acet-acetic ether *appeared* to be more difficultly soluble, when prepared in ether solution, or with dry sodium ethylate, than when prepared according to Elion's method. It is perfectly obvious that there was no connection between this experimental observation and the two sodium-acet-acetic ethers which I supposed the known product to consist of.

Nef connects these statements on his own responsibility, then misstates me in assuming the existence of an *insoluble* sodium derivative, and finally asserts that my views on the chemical processes of the acet-acetic ether syntheses must be wrong, because an insoluble derivative does not exist.[3] It is somewhat difficult to imagine a greater confusion of ideas, but, what is still more surprising, it will be shown farther on that Nef has not hesitated to publish as new a good part of the very views he condemns. On page 58 we are informed that alkyl halides should act more readily on the copper, lead and mercury derivatives than on the sodium acet-acetic ether, as the replacing of metal by alkyl takes place more readily with the lead and silver derivatives of phenols and acids than with the sodium compounds. Such assertions are unwarranted, as silver derivatives of acet-acetic ether and phenol are unknown; moreover, only complicated basic lead and mercury compounds of phenol exist, which have never been examined in their behavior towards alkyl halides, and, finally, there are no facts known justifying the assumption that lead in the salts of organic acids is replaced more easily than sodium or potassium. If such considerations have led Nef to believe that the action of alkyl halides on sodium acet-acetic ether only can take place by addition he has obviously reached it through

[1] J. prakt. Chem. **37**, 488. [2] Ibid. 478. [3] Loc. cit. 56.

ignorance of the literature on the subject. The hypothesis that the reaction takes place by addition is, however, one of the most essential points in my previous explanations, and Nef has not only borrowed this from my paper without acknowledgment, but the explanation he gave of the formation of dialkyl-acet-acetic ethers is exactly what I had assumed before him.

In the syntheses of mono-alkyl derivatives our views differ after addition has taken place, and the difference is well explained by the following equations:[1]

I.
$$CH_3-\dot{C}ONa-\dot{C}H-COOC_2H_5 + C_2H_5I =$$
$$++ \quad - \qquad\qquad + -$$
$$CH_3-C\begin{matrix}\diagup ONa \\ \diagdown I\end{matrix}^{+}_{-} - \begin{matrix}C_2H_5 \\ | \\ CH\end{matrix} -COOC_2H_5 =$$
$$CH_3-CO-\begin{matrix}C_2H_5 \\ | \\ CH\end{matrix}-COOC_2H_5 + NaI.$$

II.
$$CH_3-CONa=CH-COOC_2H_5 + C_2H_5I =$$
$$CH_3-C\begin{matrix}\diagup ONa \\ \diagdown I\end{matrix}-\begin{matrix}C_2H_5 \\ | \\ CH\end{matrix}-COOC_2H_5 =$$
$$CH_3-CONa=\begin{matrix}C_2H_5 \\ | \\ C\end{matrix}-COOC_2H_5 + HI.$$

In view of the fact that compounds containing hydroxyl and halogen combined with the same carbon are generally believed to be incapable of existence, as this group decomposes at once into halhydric acid and carbonyl, it is of interest to learn why Nef has made such an entirely improbable suggestion that, not only does ONa and I exist in combination with the same carbon,[2] but that hydriodic acid splits off, instead of sodium iodide, under conditions which are without a precedent among the known instances of the formation of unsaturated acids or their ethers. Nef[3] found that a small quantity of dibenzyl-

[1] I. is according to the writer and II. is Nef's conception.

[2] How impossible this conception is may be seen from the recent experiments with mandelic nitrile by H. A. Michael and J. Jeanpretre (Ber. d. chem. Ges. 25, 1679), who showed that even the compound $C_6H_5-CH<^{ONa}_{CN}$ cannot be obtained, as it immediately splits into benzoic aldehyde and sodium cyanide.

[3] Loc. cit. 118.

acet-acetic ether is formed when benzyl chloride acts on sodium acet-acetic ether in alcoholic solution, and claims that this fact can only be explained by assuming that sodium benzyl-acet-acetic ether is a direct product of the reaction, and benzyl chloride acts on a certain number of molecules before the chlorhydric acid has an opportunity to react, although the acid must have just separated from these molecules. The innate improbability of such a conception would be sufficient in itself to condemn it, even though facts were known that appeared to give it support. However, the formation of dibenzyl-acet-acetic ether is very easy to understand, as a stage must exist in this reaction when there is relatively a great deal of benzyl-acet-acetic ether and but little sodium acet-acetic ether present, and our present knowledge of the action of mass, or the division of a base in a mixture of acids, shows that under such conditions some sodium benzyl-acet-acetic ether would be formed and the corresponding amount of acet-acetic ether set free, and the sodium derivative would then react with benzyl chloride. It is hardly necessary to call attention to the fact that the more positive the introduced radicle is, the less di-product should be formed.

From pages 63 to 71 Nef considers the constitutions of free acet-acetic and malonic ethers, and a collection of contradictory ideas, supported by inaccurate experimental observations, are stated, such as are, fortunately, seldom seen in a chemical paper. We are informed that phenols act on aromatic amines with the same ease as on aldehydes or ketones, and are referred to Minunni's work,[1] who heated aniline phloroglucinol and calcium chloride for eight hours to 210°, but Nef is evidently unacquainted with the recent literature on phloroglucinol, or he would have known that the conception which best explains the apparent dual nature of this substance is in considering it as a ketone. The formation of a very unstable addition-product of bromine and acet-acet-anilide proves beyond doubt, according to Nef, its constitution as $CH_3—COH=CH—CONHC_6H_5$. Acetic acid unites with bromine to form a stable addition-product, which decomposes at 100° into bromacetic and bromhydric acids. Keptinic ether also unites with bromine to form very unstable bromine addition-product, and must therefore, according to Nef, be an unsaturated compound; but acetic ether forms a comparatively stable addition-product

[1] Ber. d. chem. Ges. **21**, 1984.

with bromine, and as no chemist, to my knowledge, has ever called acetic acid or its ether unsaturated compounds on account of this property, there is far less reason to attach any importance whatsoever to the supposed addition-products of bromine to acet-acet-anilide[1] and keptinic ether.

On page 66 Nef states that methyl- and ethyl-acet-acetic ethers may be converted, in ethereal solution, into their sodium derivatives absolutely without reduction, while diethyl-acet-acetic ether, under similar conditions, is partially reduced. These assertions seemed to me very doubtful, as I had repeatedly prepared the above sodium derivatives and had never obtained the required amount of hydrogen, but, as Nef draws important conclusions regarding a structural difference between ethyl- and diethyl acet-acetic ether from this result, it seemed of sufficient interest to partially repeat his experiments. The ethyl-acet-acetic ether used was a perfectly pure product, obtained by distillation *in vacuo* as already described.

The three experiments were made in the same manner, viz. by distilling off pure and anhydrous ether from sodium. Then the required amount of granulated sodium was added, and the flask, connected with a cooler and a drying tube, allowed to stand 10 hours, when the ethyl-acet-acetic ether was gradually added through a drop-funnel. In all these operations the greatest care was observed to keep the mixture perfectly dry.

I. 1.3 grams sodium under 70 grams ether (slight excess, 1.16 grams being the theoretical quantity) and 8 grams ethyl-acet-acetic ether gave 400 cc. hydrogen at 20° and 735 mm. pressure.

II. 1.2 grams sodium under 50 grams ether and 7 grams ethyl-acet-acetic ether gave 380 cc. hydrogen at 23° and 742 mm.

III. 2.8 grams sodium under 80 grams ether and 16 grams ethyl-acet-acetic ether gave 840 cc. hydrogen at 16° and 748 mm. A slight amount of sodium remained after the reaction had ceased, which gave off hydrogen, when brought into water, corresponding to 0.4 gram sodium, so that the amount of sodium which entered into the reaction was almost that required by theory.

For comparison, ten grams of ethyl-acet-acetic ether will be taken as the unit, and the above stated results will be calculated with reference to that amount:

[1] Nef calls this compound acet-acetic ether anilide, obviously a misnomer, as there is a connection between the constitutions of these compounds and their chemical names. Acetic ether anilide, to mention an analogous instance, is not used instead of acet-anilide.

Theoretical quantity of H at 0° and 760 mm.	Found at 0° and 760 mm.		
	I.	II.	III.
706.5 cc.	480 cc.	512 cc.	503 cc.

It is very evident from these results that a partial reduction must have taken place, and this fact was easily confirmed by the examination of the product of the reaction. The ethereal solutions were treated with cold water, the alkaline solution immediately extracted with ether, the aqueous residue then acidified and again extracted with ether. On fractionating the last ether-extract a small amount of an acid was obtained, boiling at about 200°, which had the characteristic odor of the higher unsaturated, monobasic acids; and discoloration took place immediately when it was dissolved in carbon disulphide and bromine added, an addition-product being formed without any evolution of bromhydric acid. As the acid also gave the permanganate test, there was no doubt that a reduction takes place in the action of sodium on ethyl-acet-acetic ether. It is not improbable that the ether of an hydroxy acid was first formed, which decomposed on heating to an unsaturated acid, and this was partially saponified by the treatment with alkali, and indeed the regained ethyl-acet-acetic ether was far from being a pure product, as it began to boil under 170°, and between that temperature and 194° over 15 per cent. passed over. I did not examine the lower-boiling portion any further than to notice that it decolorised bromine without formation of bromhydric acid, which indicated the presence of an unsaturated body in it. Nef's conclusion in regard to a structural difference in the constitution of ethyl acet-acetic ether and the diethyl-derivative is therefore drawn from inaccurate work and has absolutely no foundation.

I find also another incorrect statement in regard to ethyl-acet-acetic ether in Nef's paper, which is that a dilute solution of sodium hydrate extracts that substance from its ethereal solution. Geuther[1] had already shown that ethyl-acet-acetic ether does not dissolve in dilute aqueous alkalies, a statement which Nef therefore puts in doubt. However, Geuther's observation is absolutely correct, as ethyl-acet-acetic ether is only slightly soluble in aqueous alkalies, as it is in water, and ether extracts it from this solution; but if such a solution is allowed to stand, the ether quickly decomposes it into ketone and carbonate. Aqueous alkalies are

[1] Ann. Chem. (Liebig) **244**, 194.

able to extract ethyl-acet-acetic ether completely from its ethereal solution if shaken with it sufficiently long, but the ether is completely decomposed in this treatment.

My experience with the quality of Nef's work on acet-acetic ether had prepared me for experimental errors, but I must confess to astonishment when I came to repeat his experiments regarding the non-action of sodium on dry malonic ether. This ether boils at 195° without decomposition, and there is, therefore, no reason why such a high-boiling liquid should contain even a trace of water or alcohol; moreover, I had repeatedly made sodium malonic ether from a product which had been prepared by repeated fractionation *in vacuo*. According to Nef,[1] malonic ether should not act on sodium, as it is not a carbinol derivative like acet-acetic ether, and he found this to be the case with a product that was allowed to stand for several days with silicium chloride, and then the excess of that reagent driven off by heating the mixture to 130°. This is one of the surest methods of rendering malonic ether impure that the writer is aware off. When pure malonic ether, obtained by fractionating in a vacuum, was mixed with freshly distilled silicium chloride, in such a manner as to avoid the absorption of any moisture from the air, there was no evolution of chlorhydric acid, even if it was allowed to stand for some time, which shows such an ether to be free of water and alcohol; but it was impossible to remove the chloride by heating without the evolution of chlorhydric acid, as it acted on malonic ether, forming a very high-boiling silicium compound. The mixture after heating to 130°, as Nef did in his experiment, still contained a very considerable quantity of unchanged silicium chloride, besides partially decomposed malonic ether, the high-boiling silicium compound, and free chlorhydric acid. Although it was evidently of no importance whether such a mixture was acted on by sodium or not, I tried this experiment and noticed a brisk evolution of hydrogen. It was thought that, perhaps, by heating this mixture of malonic ether and silicium chloride in a vacuum the formation of chlorhydric acid and the high-boiling silicium product might be avoided, and the experiment was repeated, distilling off under 20 mm. pressure and only heating the flask to 50°, but even at that temperature, although the residue was far more free of silicium chloride than when heated to 130° under ordinary pressure, a constant evolution

[1] Ann. Chem. (Liebig) **266**, 67.

of chlorhydric acid was noticed and some of the high-boiling silicium compound was formed,[1] but not nearly as much as under the conditions of Nef's experiment. This residue was also acted on by sodium in ethereal solution. Pure malonic ether is therefore acted on by sodium, and the conclusion which Nef has drawn from his inaccurate work is evidently wrong.

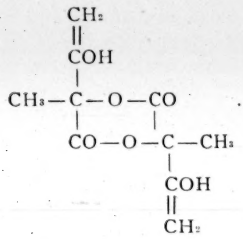
On page 61 the statement is made that the group $COOC_2H_5$ *is less negative than acetyl*, and only six pages farther on we find that if "one considers the ketone constitution of acet-acetic ether and the ordinary structure of malonic ether, then the CH_2 of the last compound must have more developed acid properties than in acet-acetic ether." Although it is interesting to know that by simply considering constitutions more or less acid properties follow, it is somewhat surprising to find that in the present instance the reason depends on $COOC_2H_5$ *being more negative than acetyl!* And again, on page 112, we are told that his considerations must be correct "because $C_2H_5O—CONa=CH—COOC_2H_5$ is more negative than $CH_3—CONa=CH—COOC_2H_5$." If this, in itself almost unintelligible assertion, be correct, will Nef explain why sodium malonic ether is so unstable that it is decomposed by water, while sodium acet-acetic ether is a stable substance? On page 103 it is stated that considerable tri-acetyl-acetic ether is formed when acetyl chloride acts on copper acet-acetic ether, and on page 110, that chlorcarbonic ether acts on the same salt only to form a mono-substitution product. If Nef's theorising were correct, exactly opposite results should be obtained. On the same page, a reason for the formation of acet-malonic ether only from copper acet-acetic ether is found in the less basic character of copper in comparison to sodium, but referring to pages 102 and 103 we see that the best way of preparing tri-acet-acetic ether is to take copper acet-acetic ether, as the sodium derivative gives mostly the di-acet-acetic ether and comparatively only a very small amount of the tri-acet product!

Finally, I shall call attention to a few more illustrations of the very incomplete knowledge of the literature of the subject on which Nef has based his speculations. On page 69, a perfect understanding of the decomposition of acet-acetic ether by dilute and concentrated alkalies is stated to have been finally gained,

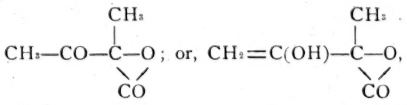
[1] It is my intention to examine the products formed in the action of silicium chloride on malonic ether.

although the reasons given are those of Geuther. On page 104, the slight difference between the boiling-points of di-acet-acetic and tri-acet-acetic ether is stated to be due in part to the presence of unsaturated carbons in the first compound, and it is further stated that a double link increases a boiling-point. This is rather difficult to understand, as tri-acet-acetic ether is not a reduction product of the di-acet compound, and, moreover, the broad statement that unsaturated carbons increase the boiling-point of a substance is incorrect, as in some cases with organic ethers and acids there is no appreciable difference, and with other classes of compounds, as is the case with ethyl and propyl alcohol, the boiling-point is lowered by unsaturation. On page 135 the experiment of Friedländer and Weinberg[1] on the formation of ethyl-carbostyrils is explained by assuming an addition as well as substitution when the sodium carbostyril is used, and only substitution when the silver derivative is used. If Nef had been acquainted with the subsequent research of Friedländer and Müller[2] he would have realised that such an explanation does not agree with their results, and if he had referred to my paper, published in 1888, he would have found that the constitution of sodium and silver carbostyril he assumed as new was suggested there, and that Friedländer's results had been explained. The possibility of obtaining carbon-homologues of phloroglucinol by the action of alkyl iodide on the sodium derivative was also predicted in the same paper, before Herzig and Zeisel's work on this subject was published, and explained by addition, as Nef does so much later. In his explanation of the formation of nitriles and isonitriles Nef assumes silver and potassium cyanides to have the constitutions Ag—N=C and K—N=C. That these structures are improbable may be shown by a number of reactions, as, for instance, the formation of CH_3—CO—CN from CH_3COCl in AgCN. From his experiments on the brom-alkyl-acet-acetic ethers Nef concludes that the constitution I suggested for tetrinic acid, which Cornelius and Moscheles afterwards confirmed experimentally, is incorrect, since the compound is formed from α-brom-methyl-acet-acetic ether and melts too high to have such a simple constitution. Nef therefore believes it to be a lactide with the structure

[1] Ber. d. chem. Ges. **18**, 1529. [2] Ibid. **20**, 2069.



In regard to the melting-point of tetrinic acid I will state that there is no defined relation known at present between this property and the chemical constitution of a substance. How wrong any conclusion drawn from such a property may be is shown in the present instance, as Moscheles and Cornelius[1] have taken the molecular weight of pentinic ether and found it agreed with that required for an ethyl derivative of the constitution I suggested. Nef's lactide constitution must therefore be wrong, and tetrinic acid should therefore have the structure

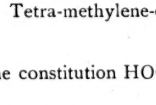


on account of the strong negative nature of the lactide group. Such a suggestion for the constitution of tetrinic acid shows, what is already evident from all of Nef's speculations, that he never understood the reasons why acet-acetic ether and analogous substances have acid properties, as he himself found that $CH_3—CO—C\begin{matrix}(COC_6H_5)_2\\ COOC_2H_5\end{matrix}$ is a neutral body, and the negative influence which acetyl in it is subjected to is incomparably greater than that of a "lactide ring." However, in regard to Nef's work on the action of bromine on acet-acetic ether, its alkyl and the sodium derivatives, it is perfectly evident that the conclusions he has drawn are not substantiated by his work even if it were accurate, but as Hantzsch[2] has already shown that the part relating to ordinary brom-acet-acetic ether cannot be correct and has

[1] Ber. d. chem. Ges. **22**, 243. [2] Ibid. **25**, 732.

announced his intention to discuss this part of Nef's work, it is not necessary to enter further on this subject.[1]

I shall take this opportunity of replying to several other criticisms of my former research on sodium acet-acetic ether. Elion,[2] misinterpreting my remarks on the solubilities of sodium acet-acetic ether that I prepared by different methods, concludes that I worked with impure sodium acet-acetic ether and, therefore, that it is a matter of doubt whether carb-ethoxyl-acet-acetic ether is really formed from sodium acet-acetic ether. Elion states that my sodium acet-acetic ether was insoluble in ether, but I never made such a statement and simply mentioned that it is pretty (*ziemlich*) insoluble, and Elion's pure product is only soluble in forty parts of ether. If Elion had read my paper more attentively his remarks would have been unwritten, as it is expressly stated that I prepared carb-ethoxyl-acet-acetic ether from sodium acet-acetic ether made in absolute alcoholic solution,[3] and, besides, the large yield obtained made formation of the substance from a partially decomposed sodium acet-acetic ether quite out of the question.

The same remarks apply with greater force to the criticisms of Freund and Gudeman,[4] who ascribed to me a constitution for tetra-methylene-carboxylic acid which I never stated, and then go on to show that their experiments make such a constitution improbable. Tetra-methylene-dicarboxylic acid, according to my views, has the constitution  , but nowhere in my paper have I given a constitution for the monobasic acid, although Freund and Gudeman might have easily inferred it if they had compared the decomposition of the so-called tetra-methylene-dicarboxylic and acetyl-trimethylene-carboxylic acids on heating. As the latter compound is stated to give acetyl-trimethylene ($CH_3—CO—\dot{C}H—CH_2—\dot{C}H_2$), it is evident that tetra-methylene-dicarb-oxylic acid would give $\dot{C}H_2—CH_2—\dot{C}H—COOH$, and there

[1] Nef was also not justified in drawing from Haller and Held's synthesis of citric acid the conclusion that chlor-acet-acetic ether is solely a γ-derivative, as these chemists only claimed that it consisted of a γ- as well as of an α-product, and Hantzsch and Schiffer (Loc. cit. 728) have now shown that it is solely an α-derivative.

[2] Ber. d. chem. Ges. **23**, 3124.

[3] J. prakt. Chem. [2] **37**, 474.

[4] Ber. d. chem. Ges. **21**, 2693.

are at present no results which disprove such a conception of its constitution.

Theoretical Considerations on the Constitution of Sodium Acet-acetic Ether and Analogous Compounds.

No hypothesis on the constitutions of acet-acetic ether and its sodium derivative can be upheld, unless every known fact concerning these substances is explained by it in a satisfactory manner; and, in the opinion of the writer, this is only possible by considering the free ether as a ketone and the sodium compound as a derivative of a carbinol.

In regard to the ketone constitution of acet-acetic ether the writer[1] has previously shown that the two facts which appeared contradictory are easily brought into accord with it, and it is only necessary to consider two new facts which are found in Nef's paper.

Von Baeyer and Kochendoerfer[2] showed in 1889 that the condensation-product from phloroglucinol and phenylhydrazine is not a hydrazone but a hydrazo-compound, and von Baeyer[3] has recently proven that this is also the case with the succin-succinic ether derivatives. He explains the reaction by assuming in the first place the formation of an unstable hydrazone, which then passes over into the stable hydrazo-derivative:

$$\underset{\text{I.}}{CH_3{-}\overset{\overset{N-NH-C_6H_5}{\|}}{C}{-}CH_2{-}COOC_2H_5} = \underset{\text{II.}}{CH_3{-}\overset{\overset{NH-NHC_6H_5}{|}}{C}{=}CH{-}COOC_2H_5}$$

It was evident that the constitution of all the phenylhydrazine derivatives of analogous compounds became an open question, and Nef[4] has since shown that the compound from phenylhydrazine and acet-acetic ether gives results analogous to those obtained

[1] J. prakt. Chem. **37**, 479-482. [2] Ber. d. chem. Ges. **22**, 2189. [3] Ibid. **24**, 2687-2698.

[4] Ann. Chem. (Liebig) **266**, 74. Nef calls the substance acet-acetic ether hydrazide, which is a wrong name, as hydrazides are only formed from hydrazines by replacing hydrogen by acid radicles. The presence of two imide groups in the substance is certainly not proven by the results he obtained by the action of acetyl chloride on it, as the carbon estimation he gives agrees better with that of a mono-acetyl than with his supposed diacetyl product:

Theory for $C_9H_{10}N_2(COCH_3)_2$.	$C_9H_{11}N_2(COCH_3)$.	Found.
67.24	69.4	69.38
6.90	7.3	6.90

It is not improbable that the compound has a different constitution than that which Nef assigns to it, as a difference of two per cent. in carbon seems too great to be ascribed to error in analysis.

by von Baeyer, and, therefore, is probably not a hydrazone, but a hydrazo-derivative as expressed by II. He concludes from this result that the only experimental fact in favor of the ketone constitution of acet-acetic ether has thereby become invalid.

Von Baeyer in his explanation called attention to the mobility of the methylene-hydrogen in acet-acetic ether, and, as the azo group has a strong affinity for hydrogen, it is not in the least surprising that this affinity should cause one of the mobile methylene-hydrogens to pass over to nitrogen; in other words, an intra-molecular reduction takes place. This not only seems probable, but has been proven actually to take place in an analogous reaction, as Japp and Klingemann [1] have shown that the product of the action of diazo-benzene chloride on sodium methyl-acet-acetic ether is not

$$\begin{array}{l} \dot{N}\text{—}\dot{N}C_6H_5 \\ | \\ CH_3\text{—}CH\text{—}COOC_2H_5, \end{array}$$

but the hydrazone of pyruvic acid, $\begin{array}{l} N\text{—}NHC_6H_5 \\ | \\ CH_3\text{—}C\text{—}COOH \end{array}$. This intra-molecular reduction is the result of the same tendency, inasmuch as the azo-compound, which is probably formed at first, takes all the mobile hydrogen available and passes over into a partially reduced group. Fully admitting the possibility of this explanation of von Baeyer, it seems to me that facts are known which indicate a different explanation of this reaction as probable. The formation of hydrazones from aldehydes and ketones and phenyl-hydrazine is generally believed to be the direct result of a condensation, water being split off; but such a procedure is unlikely, to judge from analogous reactions. The formation of crotonic aldehyde by condensation of aldehyde is preceded by that of aldol;[2] in the synthesis of aldehydes and carbonyl acids with aromatic hydrocarbons by dehydration a similar reaction probably occurs, and in fact has been shown to take place in several instances. With acet-acetic ether there are fortunately results known that leave but little doubt on the subject, as the intermediate products have been isolated. Collie [3] has shown that ammonia and acet-acetic ether unite to form the compound $CH_3\text{—}C\begin{array}{l} NH_2 \\ OH \end{array}\text{—}$

[1] Ann. Chem. (Liebig) **247**, 190. [2] Michael and Kopp: This Journal **5**, 182.
[3] Ann. Chem. (Liebig) **226**, 298.

$CH_3—COOC_2H_5$ by addition, which decomposes, even at 0°, splitting off water and forming $CH_3—CNH_2—CH—COOC_2H_5$. Still more decisive are Kuckert's results[1] with methyl-amine and di-ethyl-amine, as with the primary base a crystalline addition-product was obtained which gave off water at ordinary temperature, and the secondary base gave a yellowish liquid, probably the addition-product, which decomposes into water and $CH_3—\overset{\displaystyle N(C_2H_5)_2}{\overset{|}{C}}—CH—COOC_2H_5$. These experiments indicate that when the ketone-carbonyl of acet-acetic ether acts on bases the primary product of the reaction is an addition. The elimination of water from such an addition-product may take place in two directions, the carbinol-hydroxyl uniting either with a hydrogen joined to nitrogen or with one of the methylene-hydrogens, forming accordingly a hydrazone or hydrazo-compound. Kuckert's results with di-ethyl-amine and von Baeyer's experiments show that it is the methylene-hydrogen that enters into the reaction, and, according to this interpretation, the reaction between phenylhydrazine and acet-acetic ether should be represented as follows:

$$CH_3—CO—CH_2—COOC_2H_5+NH_2—NH—C_6H_5=$$
$$CH_3—C<\begin{matrix}NH—NHC_6H_5\\OH—CH_2—COOC_2H_5\end{matrix}=$$
$$CH_3—\overset{\displaystyle NH—NHC_6H_5}{\overset{|}{C}}—CH—COOC_2H_5+H_2O.$$

It will be seen that the formation of a hydrazo-derivative, and not a hydrazone, is in strict analogy with what is known in the action of bases on acet-acetic ether, and the obtained result tends to confirm rather than disprove the ketone constitution. Our present knowledge of the subject fully justifies the following hypothesis: *If a compound* HX *acts on a substance containing carbonyl* (=CO) *with the elimination of water, such a reaction always takes place in two phases, the first of which consists in the addition of the most reactive hydrogen of* HX *to the carbonyl-oxygen, and of* X *to the carbonyl-carbon:* $CO+HX=C<\begin{matrix}OH\\X\end{matrix}$.

Water may then split off in different ways: first, within the

[1] Ber. d. chem. Ges. **18**, 618.

molecule, as is the case in the above-described reaction of acet-acetic ether; secondly, several molecules of the addition-product may condense; and thirdly, a reagent with a reactive hydrogen may be present and this hydrogen unite with the hydroxyl of the addition-product. The conditions when one or the other of these three possibilities will happen may be generally foreseen, and I shall return to this subject at another opportunity.

The other point in Nef's paper that needs further consideration is the formation of di-substitution-products in the action of acetyl and benzoyl chlorides on sodium acet-acetic ether, whereas Elion[1] and Nef were unable to obtain a tri-acet-acetic ether by the action of acetyl chloride on sodium di-acet-acetic ether. To explain this Nef adds a second hypothesis to one that I have already shown to be impossible. In the moment when hydrochloric acid splits from $CH_3-C(ONa)(Cl)-CH<^{CO-CH_3}_{COOC_2H_5}$, the double bond must be more active than afterwards, and therefore, although sodium di-acet-acetic ether does not add acetyl chloride when once formed, it may do so at the moment of formation. This is another of those peculiar results of the double-bond hypothesis which crop out from time to time, only to be forgotten.[2] Our present knowledge of the real nature of the so-called double bond is almost limited to the manifestations of its properties, namely, that it possesses a most remarkable tendency towards saturation, so strong indeed that it often causes the separation of molecules in order to unite with the component parts, and that it is totally different in its nature from the so-called single bond. Double linkage exists only as a name, and there are absolutely no facts known which justify assuming that at the moment of unsaturation the carbons have a greater additive power than afterwards. However, such a difference as Nef claims to exist would be readily explained by my hypothesis.

Di-acet-acetic ether having stronger acid properties than acet-acetic ether, acts therefore on the sodium acet-acetic ether present, forming sodium di-acet-acetic ether. The latter sodium derivative

[1] Elion (Recueil trav. chim. **3**, 263) seems, however, to leave it a matter of doubt whether a tri-acet-acetic ether is formed or not, and Nef states that he confirmed Elion's results. It is very desirable that Nef should give a more decisive proof that the compound is tri-acet-acetic ether, as his analyses are almost 1 per cent. too low in carbon and hydrogen.

[2] This Journal **5**, 194. Demole ascribed a greater volatility to one of the dibromethylenes, for the reason that the carbons in it were not linked.

has, at first, the unstable constitution $CH_3—CO—\underset{\underset{CO—CH_3}{|}}{C}Na—CO_2C_2H_5$,

which immediately passes over into the stable form $CH_3—CONa—\underset{\underset{CO—CH_3}{|}}{C}—COOC_2H_5$. But, if a reagent is present, as is acetyl chloride in the case in question, which reacts on sodium when it is joined to carbon, it is easy to understand how a certain amount of tri-acet-acetic ether will be formed by substitution. When once the stable sodium di-acet-acetic ether is formed an addition would take place with difficulty, owing to the, relatively, very negative condition of the unsaturated carbons, and a reaction would, probably, only take place by substitution, in which case the isomeric compound

$$CH_3—\overset{\overset{O—COCH_3}{|}}{C}—C<\begin{matrix}COOC_2H_5\\CO—CH_3\end{matrix}$$

should be formed.[1] A difference in the behavior of such sodium derivatives at the moment of formation and when they have assumed their stable form, follows directly from my hypothesis, and if Nef's results are correct I can but consider them as strong evidence in its favor.

In regard to the constitution of sodium acet-acetic ether as $CH_3—CONa—CH—COOC_2H_5$, such an assumption is absolutely necessary to explain the facts, which the writer has described, on the action of chlorcarbonic ether on it, and analogous constitutions for the alkyl homologues. Among the other facts which make such a constitution probable are the formation of a dihydrofurfuran derivative in the reaction between ethylene bromide and sodium acet-acetic ether, and the difference in the behavior of free acet-succinic ether and its merotropic sodium derivative towards phenylhydrazine.

If, indeed, only the reactions of acet-acetic ether and its sodium derivative were considered the merotropic constitutions of these compounds might be considered as established with a considerable degree of certainty, but the recent researches of Claisen and von Pechmann on analogous compounds again open the subject

[1] Elion, indeed, found that acetyl chloride acts on sodium di-acet-acetic ether, but with difficulty. The reaction will be studied to see whether an isomeric product can be isolated.

for discussion. Claisen[1] found that the so-called formyl-camphor has strong acid properties; gives with acetic anhydride an acetyl product, in which acetyl is connected with oxygen, and its sodium derivative does not give a carbon-homologue with ethyl iodide, but a derivative in which ethyl is joined to oxygen. This chemist also showed that formyl-phenyl-acetic ether and acetic anhydride react to give an acetic ether, and concluded from these results that formyl-camphor and other similar formyl compounds in reality do not contain formyl, but are derivatives of unsaturated carbinols. Thus formyl-phenylacetic ether, according to this conception of Claisen, has the constitution $C_6H_5—\overset{\overset{CHOH}{\|}}{C}—COOC_2H_5$. These results have been confirmed by von Pechmann,[2] who has examined the behavior of the fatty formyl-acid ethers towards acetic anhydride, and that of their sodium derivatives towards acetyl and benzoyl chlorides, and obtained compounds in which the acid radicles are undoubtedly united with oxygen. Von Pechmann believes that the results of a comparative study of acet-acetic ether and of the analogous formyl-acetic ether will easily prove the constitution of acet-acetic ether, and having only the behavior of the above substances and of their sodium derivatives towards acetic anhydride and acetic chlorides in view, concludes that acet-acetic ether has the ketone-constitution, that its sodium derivative is formed by replacing a methylene-hydrogen by metal, and this form is stable, while formyl-acetic ether has the constitution $HOCH=CH—COOC_2H_5$.

In reaching this conclusion regarding the ketone-constitution of sodium acet-acetic ether, von Pechmann, accepting Nef's experiments on carb-ethoxyl-acet-acetic ether as correct, has therefore reasoned without considering the one reaction of sodium acet-acetic ether that shows such a constitution to be impossible. If the behavior of sodium acet-acetic ether and its homologues towards chlorcarbonic ether had alone been studied, the results obtained would quite as fully justify the conclusion that sodium in these compounds is joined to oxygen, as the results obtained by von Pechmann on sodium formyl-acetic ether do as regards that compound; especially as the difference in the behavior of acetic anhydride towards acet-acetic and α-formyl-propionic ethers

[1] Chem. Centrbl. **61**, 878. [2] Ber. d. chem. Ges. **25**, 1040.

does not, as von Pechmann supposes, justify his conclusion of the latter compound being an alcohol. I[1] have before pointed out that the formation of an acetate by the action of acetyl chloride, or acetic anhydride, on certain ketone and formyl-acids does not imply the existence of a carbinol in such compounds, as it may be the result of an addition to carbonyl and splitting off of chlorhydric or acetic acid. The addition of acetyl chloride and acetic anhydride to aldehydes is a well-known fact, and the ease with which such additions take place appears to increase with the relative negativity of the carbonyl. When the formyl-hydrogen of an aldehyde is replaced by the more positive alkyl to form a ketone, the carbonyl in such a compound is obviously relatively less negative than in the corresponding aldehyde, and, accordingly, there is less tendency on the part of acetyl chloride or acetic anhydride to add to such a carbonyl; but if the negative carboxyl is introduced into a ketone in such a position as to render the ketone-carbonyl sufficiently negative, an addition may take place with the ketone acid thus formed, especially if the carbonyl and carboxyl are in such position that stable acetates may be formed by elimination of chlorhydric or acetic acid. In succinylo-succinic ether the negativity of the ring, loosening of the α-methylene-hydrogen by carb-ethoxyl, and the tendency of reduced benzene derivatives to pass over into a less reduced state, are conditions that cause the formation of an acetate from this ketone-ether; with levulinic acid it is the introduction of carboxyl to carbonyl in the γ-position, and the possibility of the formation of a stable lactone derivative, that induces the acetate formation; whereas levulinic ether does not react with acetic anhydride, because a lactone formation would imply the separation of ethyl and oxygen and, moreover, carb-ethoxyl is not as negative as carboxyl. But the power of acetic anhydride to unite with aldehydes is not a matter of doubt, and this addition should take place very readily with a compound like formyl-propionic ether, in which the formyl is more negative than in fatty aldehydes. The di-acetyl product which is first formed decomposes under the conditions of the experiment, as do almost all β-derivatives of fatty acids on heating, into an unsaturated compound, and acetic acid or an acetate:

[1] J. prakt. Chem. **37**, 480; **44**, 113.

$$OHC{-}CH{-}COOC_2H_5 + (C_2H_3O)_2O =$$
$$\quad\quad\quad

relation to the relative positivity or negativity of the introduced radicle and the influenced atoms, but it is impossible to change the absolute positions of any atoms in the negative-positive series.

The application of this hypothesis explains a number of hitherto imperfectly understood relations of organic compounds; I shall therefore consider several instances as illustrations of its use. In ethane there is, at present, no reason for considering either of its carbons to have a different negativity, but if the relatively negative carboxyl is introduced in the place of a hydrogen, the α-carbon in the compound thus formed will become relatively more negative than the β-carbon, and the affinity of the α-hydrogen for the α-carbon decreased, as compared to the affinity of hydrogen for carbon in ethane. This decrease between the affinity of α-hydrogen for α-carbon will, further, be greater than the decrease between the β-hydrogen and β-carbon, which explains Markownikoff's law on the action of halogens on propionic acid, as also the fact that in condensations it is the α-hydrogen which enters into the reaction.

Ethylene is also a compound in which the carbons may be supposed to have the same negativity, although this does not imply that the negative unsaturated carbons have not a strong affinity for each other, but any negative organic radicle introduced in the place of a hydrogen will render the unsaturated carbons more negative, and therefore decrease their affinity for negative, but increase it for positive atoms; while the introduction of a positive radicle will have exactly the reverse effect. When a negative radicle, as carboxyl, is introduced into ethylene the unsaturated carbons are no longer of equal negativity, but the α-carbon is relatively more negative than the β-carbon, and, for that reason, when an addition takes place to these unsaturated carbons, the positive part of the additive compound will unite with the relatively more negative α-carbon, and the negative part with the less negative β-carbon.

Introducing a positive radicle like methyl, in the place of a hydrogen, forms propylene, and in this compound the α-unsatur-

condition of the unsaturated carbons but also the specific affinity of the halogen has to be taken into account. I wish further to point out that in radicles like methylene the unsaturated carbons have a strong affinity for each other, and any change which makes both these carbons more negative will decrease their affinity for each other, although it may put them in a state of positive-negative contrast. If it were possible absolutely to increase the positivity of one of the carbons and decrease that of the other it is probable that their affinity for each other would be greater than in ethane, but such changes are impossible in organic transformations.

ated carbon has therefore become relatively positive to the β-carbon. When an addition of a halhydric acid to the unsaturated carbons of propylene takes place the negative halogen will unite with the relatively positive α-carbon, and the positive hydrogen with the relatively negative β-carbon. We have here a rational explanation of the empirical laws of Markownikoff and Erlenmeyer on the addition of halhydric acids to unsaturated fatty hydrocarbons and α,β-fatty acids; but, as I have previously shown,[1] the application of the negative-positive hypothesis to the question of addition not only explains it, but has a much more extended application than these empirical rules.

When carboxyl replaces a hydrogen of ethylene, we have seen that the α-carbon is more influenced by this negative radicle than the β-carbon, and, therefore, the α-unsaturated carbon of acrylic acid should have a greater affinity for the positive hydrogen of bromhydric acid than either of the carbons of ethylene; while the β-carbon of acrylic acid, being relatively negative to the carbons of ethylene, will have less affinity for the bromine, but, as the α-carbon has increased in its negativity in greater proportion than the β-carbon, it follows that acrylic acid should add bromhydric acid more easily than does ethylene. The introduction of a carboxyl into the place of an α-hydrogen of acrylic acid does not necessarily lead to an analogous result, as the α- and β-unsaturated carbons of acrylic acid are already in a relatively positive and negative state and therefore, according to the above hypothesis, will be changed to a different extent. The α-carbon of acrylic acid being relatively negative will undergo a less relative negativisation by the introduced carboxyl than the comparatively positive β-carbon; in fact there would be the same relative changes, although in less degree, as α-carbon and α-hydrogen undergo when a negative radicle is introduced. In $\overset{+}{C}H_2—\overset{-}{C}=(COOH)_2$ the unsaturated α-carbon should have a greater affinity for the hydrogen of bromhydric acid than has the α-carbon, and the β-carbon a less affinity for bromine than has the β-carbon, of acrylic acid, but it does not follow that the acid $CH_3—C=(COOH)_2$ would take up hydrobromic acid more easily than acrylic acid, because the affinity of the β-carbon for bromine may have been diminished to a relatively greater extent than the affinity of α-carbon for hydrogen increased. Whether

[1] J. prakt. Chem. **37**, 525; **40**, 171.

the introduction of a second negative radicle may, therefore, increase or diminish the additive power probably depends on the relative negativity of the introduced radicle, the more negative it is the more likely is a diminishing of the comparative additive power.

It has been shown that propylene should have a greater additive power for hydrobromic acid than ethylene, and the question arises, whether the introduction of a positive radicle like methyl in the α-position will cause a relative increase or diminution in this additive power? The effect of introducing an α-methyl into propylene on the unsaturated carbons, which were already in a relatively positive-negative state, would cause the same changes as if the β-carbon were a more negative atom than the α-carbon; in other words, the relative positivity of the α-carbon would undergo a comparatively greater increase than the relative negativity of the β-carbon would suffer a decrease. It follows that the α-carbon would have a relatively greater increase in its affinity for bromine than the decrease of the β-carbon for hydrogen, and therefore that isobutylene should have a greater additive power for hydrobromic acid than propylene.

It is of interest to see how far experimental results agree with the conclusions obtained by the application of the "positive-negative" hypothesis in regard to the addition of substances to unsaturated compounds, and I shall therefore mention a few illustrations. Ethylene does not unite with chlorhydric acid even when heated with it; propylene very slowly in the cold but more readily at 100°,[1] but isobutylene unites with chlorhydric acid in the cold,[2] and when the acid is passed through an alcoholic solution of acrylic acid it unites and etherises it to form β-chlorpropionic ether.[3] Further, ethyl-vinyl is unacted on by chlorhydric acid under the same conditions as those under which isobutylene readily unites with it to form tertiary butyl-chloride;[4] and unsymmetrical ethyl-methyl-ethylene unites with sulphuric acid under conditions that leave trimethyl-ethylene unchanged.

Before applying the positive-negative hypothesis to the reactions of acet-acetic ether and analogous substances, it will be well to call attention to the necessity, in such speculations, of comparing similar radicles, as, if they are unlike in their structure, it

[1] Berthelot: Compt. rend. **44**, 1350.
[2] Ann. chim. phys. [5] **28**, 549.
[3] Ann. Chem. (Liebig) **163**, 95.
[4] Le Bel: Compt. rend. **85**, 852.

is not permissible to infer from their constituent atoms that the unsaturated carbon of a radicle is necessarily relatively more positive or negative than that of the other radicle. It has already been shown that Nef at times considers $COOC_2H_5$ as positive to CH_3CO and again negative, although the properties of compounds containing the group $COOC_2H_5$, show, beyond doubt, that it behaves as a less negative radicle. This paradoxical conclusion may be understood when one considers that the relative negativity of the unsaturated carbons of $COOC_2H_5$ and CH_2—CO depends, not only on the negative-positive relations of the constituent atoms, but also on their distances from these atoms, and it is possible that the ethyl of $COOC_2H_5$, although united with oxygen, may have a greater positive influence than methyl, owing to its being less distant.

The application of these speculations to the problem of the reactions of sodium acet-acetic ether and analogous substances, will be more easily followed by arranging the formulas of the compounds thus:

I. H_5C_2O—CONa—CH—$COOC_2H_5$.

II. H_3C—CONa—CH—$COOC_2H_5$.

III. H—CONa—CH—$COOC_2H_5$.

IV. H—CONa—CH—C$<^{C_8H_{14}}_{CO}$.

V. H—CONa—CH—$COOC_2H_5$.

VI. H_5C_2OOC—CONa—CH—$COOC_2H_5$.

VII. CH_3—CONa—CH—$COOC_2H_5$.

VIII. CH_3—CONa—C=$(COOC_2H_5)_2$.

In sodium acet-acetic ether (II) the relations between the positivity and negativity of the unsaturated carbons are such that they are able to cause the addition of a substance like ethyl iodide, whose additive components differ considerably in their positivity and negativity, and also of a compound like acetyl chloride, both of whose parts are negative, but not strongly united. Chlorcarbonic ether may be classed between such compounds as ethyl iodide and acetyl chloride, as its halogen is considerably more firmly united to carbon than chlorine is in acetyl chloride. It is possible that, with such a compound, the additive power of the unsaturated carbons in sodium acet-acetic ether, and the tendency of the halogen to unite directly with sodium are approximating an equilibrium, in which case a part of the reaction should take place by substitution and, at the same time, a certain proportion of the

reagent should unite by addition to the unsaturated carbons. In the case of sodium acet-acetic ether it would seem as if addition predominated, since comparatively little acet-malonic ether is formed.

Sodium malonic ether (I) may be considered as formed from sodium acet-acetic ether by replacing methyl by the relatively more positive ethoxyl, and we have seen that such an interchange increases the affinity of the unsaturated carbons for negative atoms or radicles, and also increases the relative difference of the positivity and negativity of these carbons. If acetyl chloride acts on sodium acet-acetic ether by addition, it will be added still more readily to sodium malonic ether, but the relative increase in the affinities of the unsaturated carbons is also sufficient to cause the separation of the more strongly joined chlorine and carb-ethoxyl of chlorcarbonic ether, and this action is therefore solely the result of an addition.

Sodium formyl-acetic ether (III) stands in the relation to sodium acet-acetic ether that a hydrogen is replaced by the more positive methyl. In this compound, therefore, the unsaturated carbons are comparatively more negative than those of sodium acet-acetic ether, and therefore have less tendency to cause the addition of a reagent like acetyl chloride, whose additive components are both negative; and there is also a relative decrease of the additive power of the unsaturated carbons for a reagent like ethyl iodide, whose components are positive and negative, in comparison with those of sodium acet-acetic ether. Such a change favors substitution with acetyl chloride, and hence von Pechmann obtained an acetate in this reaction.[1]

Finally, to complete this series, comparing sodium formyl-camphor (IV) with sodium formyl-acetic ether, we have the replacement of the negative carb-ethoxyl in the latter compound by the more negative radicle $\begin{matrix} -C-C_8H_{14} \\ \diagdown \quad | \\ \quad CO \end{matrix}$, and its unsaturated carbons have therefore a still less affinity for chlorine and acetyl than those of sodium formyl-acetic ether. This reaction, therefore, takes place, as Claisen has shown, by substitution. The relative posi-

[1] It is probable that methyl iodide would act at least partly by addition, and this experiment will be made. Acetyl chloride acts quite readily by substitution even if the sodium is united with a negative radicle, as is seen by the formation of acetic anhydride from it and sodium acetate.

tivity and negativity of the unsaturated carbons also may have been decreased, as both the α-hydrogens are replaced by negative radicles, and in this compound a stage is reached where even ethyl iodide no longer acts by addition, but only by substitution.

In the second column we have the constitutions of sodium formyl-acetic and sodium oxal-acetic ethers, and it is evident that the unsaturated carbons in the latter compound are relatively more negative. We may therefore expect that acetyl chloride would act by substitution, although there have been no experiments in this direction. Methyl iodide acts by addition, but with difficulty and only a poor yield is obtained. In the same column sodium acet-malonic and sodium acet-acetic ether have been placed together for comparison. The former compound may be considered as formed from the latter by replacing a hydrogen by the negative carb-ethoxyl, which renders its unsaturated carbons relatively considerably more negative and may decrease their relative positivity and negativity. This substance has such a negative character, and the affinity of carbon for carbon is so loosened thereby, that neither with acetyl chloride nor ethyl iodide have derivatives of it as yet been obtained.

It appears to the writer that, however imperfect these speculations on sodium acet-acetic ether and analogous compounds may be, they afford an indication why such apparently similar products behave so differently, and at least merit attention as pointing to a method of investigating this most intricate problem. Claisen and von Pechmann have pointed out that the constitutions they assign to formyl-camphor and formyl-acetic ether would invalidate the generalisation of Erlenmeyer's law on the non-stability of vinyl alcohol and derivatives of it, and this assumption, in connection with the results described in this paper on sodium acet-acetic ether, make the constitutions they assign to their compounds appear improbable.[1]

BONCHURCH, ISLE OF WIGHT, *May*, 1892.

[1] Since the above paper was handed in for publication, two communications, touching in part on the same subject, have been published by Claisen (Ber. d. chem. Ges. **25**, 1760, 1776), in which he has called attention to some of the errors of experimentation and reasoning to be found in Nef's paper on acet-acetic ether, and has confirmed my previous view on the constitution of carb-ethoxyl-acet-acetic ether.

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON AROMATIC SILICIC ETHERS.

By H. N. Stokes.

In a paper on the action of phosphorus oxychloride on ethyl silicates and chlorsilicates[1] (chlorhydrines), I have shown that this reagent converts ethyl orthosilicate completely into ethyl chloride and silico-pyrophosphoryl chloride, $SiP_2O_6Cl_2$, and that the ethyl orthochlorsilicates yield under the same conditions these bodies and silicon tetrachloride, the amount of the latter being proportional to the amount of chlorine in the silicon compound used, the trichlorsilicate yielding most, while tetra-ethyl silicate gives none.

$$4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$
$$Si(OC_2H_5)_4 + 2POCl_3 = \quad SiP_2O_6Cl_2 + 4C_2H_5Cl.$$

It was not thought worth while to repeat these experiments with other silicic ethers of the aliphatic series, as similar results were to be expected.

In view of the different properties in general of aromatic bodies, the action of phosphorus oxychloride on silicates of this class could not be foreseen. I have therefore treated *phenyl orthosilicate*[2] with phosphorus oxychloride, and have obtained results which show in a striking manner the difference between aliphatic and aromatic silicates.

The proportion selected was that required by the equations—

$$Si(OC_6H_5)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4C_6H_5Cl,$$

or

$$Si(OC_6H_5)_4 + 2POCl_3 = SiCl_4 + 2PO\begin{matrix}Cl\\(OC_6H_5)_2.\end{matrix}$$

The mixture, after being heated 3–4 hours at 170°–180° (the temperature at which the ethyl silicates react with phosphorus oxychloride), was distilled. No indication whatever of a reaction could be discovered, the oxychloride being recovered unchanged, and proved to be absolutely free from silicon compounds. After being heated 16 hours at 240°, the liquid was somewhat discolored, but perfectly clear. On fractioning, it was easily separated into silicon tetrachloride (b. p. 59°), phosphorus oxychloride (b. p.

[1] This Journal **13**, 244; Ber. d. chem. Ges. **24**, 933.

[2] Hertkorn: Ber. d. chem. Ges. **18**, 1679.

109°), and chloride of phenyl-phosphoric acid, $POCl_2(OC_6H_5)$ (b. p. 240°–243°), with a residue consisting of chloride of di-phenyl-phosphoric acid, $POCl(OC_6H_5)_2$ and phenyl phosphate.

The fraction of b. p. 59° gave—

	Calculated for $SiCl_4$.	Found.
Si	16.47	16.24

The amount of tetrachloride was approximately equivalent to the quantity of phenyl silicate used, while the higher-boiling portions and the residue were found to be practically free from silicon, thus proving the conversion into tetrachloride to be complete. Not a trace of chlorbenzene or silico-phosphoryl chloride was formed.

It will be noticed that while the ether is completely converted into chloride, the reaction does not proceed strictly according to the second of the above equations, but that a mixture of phenyl phosphate with the chlorides of the two phenyl-phosphoric acids results, some of the oxychloride remaining unchanged.

By means of this reaction and that described previously,[1] it is easy to convert aromatic or aliphatic orthosilicates into silicon tetrachloride. The aromatic ethers, heated with phosphorus oxychloride, give the tetrachloride directly; the aliphatic ethers yield silico-pyrophosphoryl chloride, which is readily converted into silicon tetrachloride by heating with phosphorus pentachloride[2] at 100°. Phosphorus pentachloride, used directly, effects the transformation only with great difficulty. Friedel and Crafts[3] have shown that the pentachloride readily converts ethyl orthosilicate into ethyl monochlorsilicate, $SiCl(OC_2H_5)_3$. I have found that this reaction cannot readily be pushed further than the trichlorsilicate, $SiCl_3(OC_2H_5)$. This body holds the ethoxyl very firmly, and even after heating many hours at 140° with pentachloride, but little silicon tetrachloride is formed. If heated much higher, the pentachloride liberates chlorine, causing total destruction of the ether. Acetyl and benzoyl chlorides effect complete conversion into tetrachloride, but only when used in large excess and on heating at over 200° for a very long time.

I am studying the action of various metallic haloid salts, especially those of aluminium, on silicic ethers, and have observed a similar difference; aluminium chloride, for example, readily converting the aromatic ethers into silicon tetrachloride, while its

[1] This Journal **13**, 248. [2] Ibid. **13**, 247. [3] Ann. chim. phys. [4] **9**, 14.

action on aliphatic ethers is entirely different and much more complex, the products depending on the nature of the ether taken and the proportional amount of aluminium chloride used. The results will be described in a separate paper.

U. S. GEOLOGICAL SURVEY, WASHINGTON, *July*, 1892.

NOTE ON BENZYL SILICATE.

BY H. N. STOKES.

As is known, both ethyl alcohol and phenol, if perfectly anhydrous, produce with silicon tetrachloride the corresponding *ortho*-silicates in nearly theoretical amount, the chief difference being that while ethyl alcohol acts violently, with reduction of temperature,[1] phenol requires prolonged boiling for complete conversion into the ether, the evolution of hydrochloric acid being scarcely noticeable at ordinary temperature.[2]

Anhydrous *benzyl* alcohol, as was to be presumed, behaves towards silicon tetrachloride as an aliphatic alcohol, not as a phenol, violent action with fall of temperature occurring. The reaction is not smooth, however, as in the case of ethyl alcohol. A large amount, perhaps one-fourth, is converted into *benzyl chloride*, either by direct action of the hydrochloric acid evolved, or indirectly by action of the latter on the benzyl silicate. As a result, if the calculated amount of alcohol be taken, much remains unchanged, and the tetrachloride is largely converted into poly-silicates. On distilling the mixture under atmospheric pressure, some benzyl silicate passes over, but this is completely broken up by one or two redistillations. The products of decomposition consist of water, toluene, stilbene, anthracene and high-boiling products of undetermined nature. As no particular interest attaches to benzyl silicate, no further attempt was made to isolate it.

This formation of benzyl chloride recalls the action of benzyl alcohol on boron trichloride,[3] when the chief product is benzyl chloride.

U. S. GEOLOGICAL SURVEY, WASHINGTON, *July*, 1892.

[1] Ebelmen: Ann. Chem. (Liebig) **57**, 334. [2] Hertkorn: Ber. d. chem. Ges. **18**, 1679.
[3] Councler: J. prakt. Chem. [2] **18**, 396.

RESEARCHES ON THE SUGAR OF THE *AGAVE AMERICANA*.

By Gustave Michaud and José Fidel Tristan.

With the juice extracted from the stalk of the *Agave Americana*, the Mexicans make an intoxicating beverage called *pulque*. This plant is extensively grown in Mexico for this purpose; its culture is lucrative, as it grows in barren as well as in fertile grounds and requires but little care. These facts suggested to us the thought that the plant might perhaps be used industrially as a source of sugar, and this idea led us to examine the nature of the sugar contained in the Agave.

We could not obtain, at first, the stalks we wanted, and began our work with the leaves. These are thick and full of a juice that exhales a nauseous smell. We cut the leaves into small pieces and squeezed them dry with a screw-press. The juice was mixed with two volumes of 90-per cent. alcohol and left during 24 hours in a cool place; then it was filtered. The alcohol was distilled off and the aqueous residue mixed with basic acetate of lead. Care was taken to reduce to a minimum the excess of the latter reagent. After filtration, the lead was removed by a current of sulphuretted hydrogen and the filtered liquid was submitted to polarimetric examination. In spite of its sugar-like flavor it was inactive.

It reduced Fehling's solution; 0.45 cc. of the liquid being necessary to reduce 10 cc. of the reagent. According to this experiment, and admitting that the reducing power of the sugar contained in the Agave was equal to that of glucose, the solution should have contained 11.11 per cent. of sugar. But the following determination gave a result altogether different: 20 cc. of the liquid were evaporated at a low pressure to a sirupy consistency and left during a few hours in a flat saucer, upon a drying oven, in a lukewarm place. Little by little there occurred a change in the consistency and in the color, which became lighter from the margin to the centre. The solid mass was then examined with the microscope and was found to be made up of small crystals. When these were thoroughly dried their weight was 3.716 grams; this showed a concentration of 18.58 per cent.

Then 100 cc. of liquid were mixed with 10 cc. of hydrochloric acid, heated a little while at 100° C., and cooled. Submitted to polarimetric observation it gave a rotation of $-5.92°$. Its richness in sugar was determined with Fehling's solution. After the necessary reductions for dilution, it was found that it took 0.27 cc. of liquid to decolorise 10 cc. of Fehling's solution. These numbers showed a concentration 18.52 per cent., which was only a little inferior to that which could be calculated (19.55) from the concentration of the liquid previous to its inversion and such as had been shown by the evaporation of 20 cc.

From these experiments it might be inferred that the Agave contained an inactive sugar whose reducing power was about five-eighths of that of glucose, and which could be inverted and transformed into another or into various others whose rotatory power or the algebraic sum of whose rotatory powers was $=-14.53°$.

It might also have been supposed that the Agave contained not only one class of sugar but a mixture of sugars, and that the inactivity of the sugared juice was the result of an exact compensation. The following experiments showed the value of this hypothesis:

Various stalks were squeezed less than an hour after being cut. The juice was submitted to the same treatment as before, but after elimination of the lead it was concentrated, under low pressure, to a sirupy consistency; then it was treated with some animal charcoal and examined with the polarimeter. It showed a rotation of $+0.73°$. 10 cc. were evaporated to dryness. They contained 7.103 grams of sugar. These numbers showed a rotatory power of $[\alpha]_j = 0.51$. It was thought that this optical action of the syrup might not belong to the sugar that formed the bulk of it, but to an impurity such as glucose, and in order to verify this hypothesis, the sugar was purified by three crystallisations made as before, the crystalline powder being each time compressed between sheets of filter-paper. Then 39.242 grams of dry crystals were dissolved in 100 cc. of water and the solution submitted to polarimetric observation. It was inactive.

Having thus acquired the certitude of having isolated an inactive sugar in a state of purity, we proceeded to the following experiments in order to determine its most important characteristics.

Two combustions of the crystals were made; they gave the following results:

	Calculated for $C_{12}H_{22}O_{11}$.	Found. I.	II.
C	42.10	41.82	41.79
H	6.43	6.50	6.54

An aqueous solution of the Agave sugar was mixed with lime. After filtration it was verified that the liquid was precipitated by heat or by addition of alcohol. Submitted to the action of a current of carbonic acid it regenerated an inactive sugar, probably identical with the Agave sugar.

The products of oxidation of the sugar were examined for the purpose of determining the presence of mucic acid. 2 grams of sugar were dissolved in 3 cc. of water and mixed with 12 cc. of nitric acid. After it had ceased emitting nitrous vapors, the volume of the liquid was reduced by evaporation to 3 cc., then it was mixed with 15 cc. of water. The liquid remained perfectly transparent, thus showing, by this negative reaction, the absence of mucic acid among the products of oxidation.

Two solutions of pure sugar were used to determine the rotatory power of the products of inversion. After being mixed with one-tenth of hydrochloric acid they were heated at 100°, cooled and examined with the polarimeter. The following figures express the result of this determination. C = concentration = quantity of active substance dissolved in one cubic centimeter of solution, the determination being made with Fehling's solution.

	C	a	λ	$[a]_v$
I.	0.3920	−12.41	2.2	−14.390
II.	0.5035	−16.28	2.2	−14.470

The results of the preceding investigations may be stated in the following conclusions:

The *Agave Americana* contains a sugar of the formula $C_{12}H_{22}O_{11}$. This sugar differs from all other sugars of the same group, except synanthrose, by its inactivity. It differs from synanthrose by its power of crystallising, by its action in Fehling's solution, and by the rotatory power of the products of its inversion.

We propose for this sugar the name of *Agavose*.

San José, Costa Rica.

REVIEWS.

SCIENTIFIC CORRESPONDENCE OF JOSEPH PRIESTLEY. Ninety-seven letters addressed to Josiah Wedgwood, Sir Joseph Banks, Capt. James Keir, James Watt, Dr. William Withering, Dr. Benjamin Rush, and others. Together with an appendix—I. The Likeness of Priestley in Oil, Ink, Marble, and Metal. II. The Lunar Society of Birmingham. III. The Inventory of Priestley's Laboratory in 1791. Edited, with copious biographical, bibliographical and explanatory notes, by H. CARRINGTON BOLTON. New York: Privately printed, 1892. viii + 240 pp. 8vo.

Dr. Bolton deserves the thanks of chemists and others for this labor of love. The letters here presented to the public for the first time will be read with interest, and will help the present generation better to understand that remarkable man, Joseph Priestley, who seems not to have been well understood in his lifetime—even by himself. The editor of the letters remarks: "The ideal sketch of Priestley as an investigator in science is, we think, yet to be written; we do not attempt in the following pages to supply this want, but rather to contribute material for some future historian to use in such a work. The advantages afforded by letters to obtain insight into the very thoughts of their writer, and to illustrate his character, are acknowledged by all, and with this in view we have collected and annotated the correspondence which here follows." Among the most interesting of the letters are those written to Josiah Wedgwood. In regard to these Dr. Bolton says: "The previous references to these letters by no means detract from the interest attached to their present publication; they cover a period of thirteen years (1780–1792) and compose the whole of the extant correspondence between the chemist and the potter. They treat almost exclusively of scientific matters, and are written in the confiding spirit which characterised the friendly intercourse of the men of science. Priestley often sat down to write his friend while flushed with delight at the completion of a successful experiment, sometimes even before his crucibles had cooled; and feeling assured that his communications would be received by a sympathising reader, he wrote his first impressions, his hopes and his plans with a naturalness and self-portrayal pleasant to behold."

A MANUAL OF CHEMISTRY, INORGANIC AND ORGANIC, WITH AN INTRODUCTION TO THE STUDY OF CHEMISTRY. By ARTHUR P. LUFF, M. D., etc. Philadelphia: Lea Brothers & Co., 1892.

Here it is again. Possibly in the millennium there will be medical students able to comprehend the atomic theory and all

that that implies before they have learned anything about chemistry. Certainly the medical students of the present cannot do it. And why should they try? Hear this. "The formulæ of these acid radicals and their quantivalences, together with the symbols of the elements and their atomicities, must be thoroughly committed to memory; the student will then be able easily to construct formulæ, the representation of chemical reactions by means of equations is but another step forward." The student will not only be able to construct formulæ, but he will probably go on constructing formulæ under the impression that he is learning chemistry. The writer of this notice sometimes thinks, and the intervals between the thoughts are getting shorter, that if the use of formulæ were given up entirely in elementary instruction better results would be obtained. If the book under consideration is to be used by medical students, and that is what the author hopes, the first seventy pages should be omitted, and a simple, comprehensible introduction supplied by the teacher. But, even as regards the rest of the book, all that can be said is that it is "pretty good," and as, in the world to come, there is (it is stated) no room for "pretty good" people, so there is no room in this world for "pretty good" text-books on chemistry. I. R.

THE PRINCIPLES OF THEORETICAL CHEMISTRY, WITH SPECIAL REFERENCE TO THE CONSTITUTION OF CHEMICAL COMPOUNDS. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. Fourth edition, thoroughly revised. Philadelphia: Lea Brothers & Co., 1892.

"In preparing this new edition I have been tempted to change the book fundamentally and give it a character more in keeping with the recent tendencies of work in the field of Physical or General Chemistry. But, taking everything into consideration, I have concluded to resist the temptation, and remain true to the original title and character of the book. Accordingly, it is essentially what it has been—a brief treatise on those facts and speculations that have to deal especially with the problem of the constitution of chemical compounds. My object has been, and is, to help students to get clear ideas in regard to the foundations of chemistry. That the treatment has been regarded with favor is shown by the fact that four editions of the book have been demanded in a comparatively short time; and, further, by the fact that, since the appearance of the last American edition, it has been translated into German and into Italian. I believe that all changes called for by the advance of the science have been made, and that this edition will be found abreast of the times. The chief addition is a short chapter on Solutions."—*The Preface.*